ASSESSMENT OF SILVER AND TIN ATOMIC MOBILITIES IN POLYCRYSTALLINE MAGNESIUM ALLOYS

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2017
To AI
ACKNOWLEDGMENTS

First and foremost, I would like to thank God for all the blessings he has bestowed on my life, in particular the opportunity to return to the University of Florida to pursue my Master’s Degree. I would also like to thank the United States Air Force for sending me back to the University of Florida to pursue a Master’s Degree, and for covering the entire cost of sending me back to school. I want to thank my supervisors at Eglin Air Force Base, Cleo and Jack, for their patience and understanding throughout the time I’ve spent working on this project. I would also like to thank my co-workers at Eglin Air Force Base for their support and encouragement throughout the time I’ve worked towards this Master’s Degree.

I would like to thank my advisor, Dr. Michele Manuel, for all that she has done for me during both my undergraduate and graduate career here at the University of Florida. I’m grateful for all her guidance and mentorship throughout my time here, especially in professional development and in this project. I would also like to thank my committee members, Dr. Simon Phillpot and Dr. Richard Hennig, for their feedback and guidance. In addition, I would like to thank all the members of Dr. Manuel’s research group, Sujeily, Wesley, David, Oscar, Flavia, Andrew, Ellie, Brittani, Ian, and Dr. Monica Kapoor, for their help and friendship. Specifically, I would like to thank Ian for the numerous hours he spent working this project alongside me and teaching me all the techniques I needed to work on this project. I would also like to thank Dr. Kapoor for numerous hours she spent helping me edit my thesis and my thesis presentation.

I would also like to thank my longtime mentor, Dr. Rachel Abrahams, for all of her help and support over the years. From introducing me to the field of materials science
and engineering as a senior in high school to all her advice and wisdom that she gave me while I pursued graduate studies, she has been incredibly supportive and helpful. I would like to thank my parents, grandmother, and my brother, Alex, for their always constant love and support. Finally, I would like to thank all of the friends I've made while here at the University of Florida for their support, encouragement and friendship. This project would not have been possible without each and every one of you.
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LIST OF TERMS

\[ A_i^{p_j} \]
Interaction parameter

\[ v_{A_{Ag}^{Mg,Ag}} \]
Interaction parameter of Ag in Mg-Ag

\[ v_{A_{Ag}^{Mg,Sn}} \]
Interaction parameter of Ag in Mg-Sn

\[ v_{A_{Sn}^{Mg,Sn}} \]
Interaction parameter of Sn in Mg-Sn

\[ v_{A_{Sn}^{Mg,Ag}} \]
Interaction parameter of Sn in Mg-Ag

AE  
Magnesium-Aluminum-Rare Earth

Ag  
Silver

Al  
Aluminum

AM  
Magnesium-Aluminum-Manganese

Ar  
Argon

AS  
Magnesium-Aluminum-Silicon

AZ  
Magnesium-Aluminum-Zinc

BTU  
British Thermal Unit

\( C \)
Concentration

\( ^{0\circ}C \)
Degrees Celsius

\( C^* \)
Concentration at distance \( x \)

\( C^{\pm\infty} \)
Concentration at the terminal ends of the diffusion couple

\( C_i \)
Concentration of component \( i \)

\( C^0 \)
Concentration at the Matano plane

CO\(_2\)
Carbon Dioxide

CAFE  
Corporate Average Fuel Economy

CALPHAD  
Calculation of Phase Diagrams

Cd  
Cadmium
Ce  Cerium
Cu  Copper

$D$  Diffusion coefficient

$D_i$  Chemical diffusion coefficient of component $i$

$D_0$  Pre-exponential factor

$D_i^*$  Tracer diffusion coefficient of component $i$

$D_i$  Diffusion coefficient of component $i$

$D_A^I$  Intrinsic diffusion coefficient of component $A$

$D_B^I$  Intrinsic diffusion coefficient of component $B$

$D_{k,j}^I$  Lattice fixed frame of reference diffusion coefficient

$D_{k,j}^V$  Volume fixed frame of reference diffusion coefficient

$D(C^*)$  Interdiffusion coefficient of at concentration $C^*$

$dC$  Change in concentration

$dC_i$  Change in the concentration of component $i$

$d\eta$  Change in Boltzmann transformation variable

$dx$  Change in distance

$\partial C_i$  Partial derivative of concentration of component $i$

$\partial t$  Partial derivative of time

$\partial x$  Partial derivative of distance

$\partial x^2$  Partial derivative of the square distance

$\partial X_A$  Partial derivative of the mole fraction of component $A$

$\partial \mu_i$  Partial derivative of the chemical potential of component $i$

$\partial X_j$  Partial derivative of the mole fraction of diffusing species $j$

$\partial^2 C_i$  Second order derivative of the concentration of component $i$
\( \delta_{ik} \)  \hspace{1cm} \text{Kronecker delta function}

DFT  \hspace{1cm} \text{Density Function Theory}

DICTRA  \hspace{1cm} \text{Diffusion Controlled Transformations}

EDS  \hspace{1cm} \text{Energy Dispersion Spectroscopy}

EISA  \hspace{1cm} \text{Energy Independence and Security Act}

EPMA  \hspace{1cm} \text{Electron Probe Microanalyzer}

Fe  \hspace{1cm} \text{Iron}

\( \gamma \)  \hspace{1cm} \text{Interfacial free energy}

g  \hspace{1cm} \text{Gram}

g/cm^3  \hspace{1cm} \text{Grams per cubic centimeter}

g/km  \hspace{1cm} \text{Grams per kilometer}

Ga  \hspace{1cm} \text{Gallium}

GPa  \hspace{1cm} \text{Gigapascal}

HCP  \hspace{1cm} \text{Hexagonal close packed}

In  \hspace{1cm} \text{Indium}

\( J_i \)  \hspace{1cm} \text{Flux density of component } i

K  \hspace{1cm} \text{Kelvin}

kg  \hspace{1cm} \text{Kilogram}

La  \hspace{1cm} \text{Lanthanum}

LSW  \hspace{1cm} \text{Lifshitz-Slyozov-Wagner}

Log  \hspace{1cm} \text{Logarithm}

\( M_i \)  \hspace{1cm} \text{Atomic mobility of component } i

\( M_{ki} \)  \hspace{1cm} \text{Atomic mobility of component } i \text{ in gradient } k

\( M_i^0 \)  \hspace{1cm} \text{Atomic mobility frequency factor}
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<tr>
<td>Sb</td>
<td>Antimony</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>U</td>
<td>Uranium</td>
</tr>
<tr>
<td>v</td>
<td>Kirkendall (marker) velocity</td>
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<tr>
<td>$V_m$</td>
<td>Molar volume of the precipitate</td>
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<tr>
<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package</td>
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<tr>
<td>WDS</td>
<td>Wavelength Dispersive Spectroscopy</td>
</tr>
<tr>
<td>wt %</td>
<td>Weight percent</td>
</tr>
<tr>
<td>x</td>
<td>Distance</td>
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<tr>
<td>$x_0$</td>
<td>Matano plane</td>
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<tr>
<td>$X_A$</td>
<td>Mole fraction of component $A$</td>
</tr>
<tr>
<td>$X_B$</td>
<td>Mole fraction of component $B$</td>
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<tr>
<td>$X_e$</td>
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In an effort to increase fuel efficiency and decrease carbon dioxide emissions, the automotive industry is considering low-weight alternatives to the current structural materials. Magnesium (Mg) alloys are of particular interest due to Mg being the lightest structural metal. However, current Mg alloys have limited elevated-temperature applications due to poor creep resistance. The advent of computational thermodynamic and kinetic techniques allows faster and focused alloy development at a fraction of its previous cost. As an integral part of Mg alloy development, the kinetics of the Magnesium-Silver (Mg-Ag), Magnesium-Tin (Mg-Sn), and Magnesium-Silver-Tin (Mg-Ag-Sn) polycrystalline solid-solution systems were investigated.

Diffusion couples were prepared to study Ag diffusion in Mg and in Mg-Sn and Sn diffusion in Mg and in Mg-Ag, and each of these were annealed at 450, 500, and 550°C. Concentration profiles were extracted from the diffusion couples using electron probe microanalysis, and interdiffusion coefficients were calculated using the Sauer-Friese-den Broeder modification of the Boltzmann-Matano analytical method. These interdiffusion coefficients were iteratively optimized to yield kinetic data in the form of atomic mobility parameters, and were validated using additional diffusion couple
experiments. It was shown that the addition of Sn to Mg-Ag decreased the activation energy of Ag diffusion in Mg, and the addition of Ag to Mg-Sn increased the activation energy of Sn diffusion in Mg. This increase in activation energy slows Sn diffusion in Mg at temperatures below 500°C, which can improve the creep resistance of Mg-Ag-Sn alloys for use in elevated-temperature automotive applications.
CHAPTER 1
INTRODUCTION

In 2003, it was determined that 96% of the world’s transportation systems rely on petroleum-based fuels [1]. As a result, transportation systems account for about 40% of the world’s oil consumption of approximately 75 million barrels of oil per day [1]. In 2016, the United States transportation sector alone consumed 27.934 quadrillion British thermal units (BTU) of energy over the course of the year, 26.424 quadrillion BTU (roughly 95%) of which was fossil fuels such as petroleum and natural gas [2]. This consumption has been steadily increasing from the 1950s up until 2008 [2]. Within that time span, vehicle ownership in the United States has grown from about 74.4 million total vehicles in 1960 to more than 239 million vehicles in 2002, with an average annual growth rate of 3% [3].

The increased use of petroleum and other fossil fuels presents sustainability problems to the transportation sector because fossil fuels are nonrenewable sources of energy. Additionally, increased fossil fuel consumption results in increased greenhouse gas emissions. In 2015, the transportation sector accounted for 27.5% of such greenhouse gas emissions in the United States [4]. With the effect of greenhouse gas emissions on global warming understood, steps must be taken to reduce the amount of greenhouse gas emissions by the transportation industry [5].

Recently, there has been a push by the United States government to improve fuel efficiency and reduce the amount of greenhouse gases produced by the transportation industry. In 2007, the Energy Independence and Security Act (EISA) was passed, which established more stringent Corporate Average Fuel Economy (CAFE) standards [6]. CAFE standards set the minimum gas mileage that every automotive
company’s fleet of vehicles must meet in order for those vehicles to be sold in the United States. Since the passing of EISA, CAFE standards for passenger cars and light trucks have increased to 35 miles per gallon (mpg) by the year 2020, and are projected to increase to 54.4 mpg by the year 2025 [7,8].

To meet these demands of improved fuel efficiency, automotive companies have looked at improving a variety of factors. The fuel efficiency of a vehicle depends on multiple variables such as vehicle power, vehicle speed, engine and transmission efficiencies, and fuel type [9]. The vehicle power requirement, in turn, is the sum of the power needed for vehicle acceleration, driving on a grade, overcoming resistance at the tire-road interface, overcoming aerodynamic drag, and operating in-car accessories [9]. Of these, the vehicle acceleration, driving on a grade, and overcoming resistance at the tire-road interface power requirements are directly proportional to the vehicle weight [9].

As a result, reducing vehicle weight can lead to large reductions in the vehicle power requirement, which in turn can improve fuel efficiency. A 10% reduction in vehicle weight can result in an increase of 5-8% in fuel efficiency, and a 100 kilogram (kg) reduction in vehicle weight can lead to a 12.5 grams per kilometer (g/km) reduction in carbon dioxide (CO₂) emissions [9–11]. Additionally, when vehicle weight is reduced, the power needed for acceleration and braking is also reduced, which allows car manufacturers to design smaller engines, transmissions, and braking systems [9].

In order for a material to be considered as a weight-reducing alternative in automotive design, it must have a lower density than the material currently being used. At the same time, it should also achieve or improve upon the mechanical properties of the material currently being used. Of particular importance in automotive applications
are the bending stiffness and bending strength of a material [9,11,12]. These can be determined from a material’s elastic modulus and yield strength [12]. Currently, steel is used for a majority of the parts in a car, and accounts for around 55-67% of the total weight of the car [9,11]. However, the density of steel is about 7.8 grams per cubic centimeter (g/cm³), making it a limiting factor in improving the fuel efficiency of automobiles [9–11,13].

Aluminum (Al) alloys, in comparison, currently make up 8.5% of the total weight of cars, and are used in parts such as the engine block and the steering wheel [9]. Aluminum alloys have densities around 2.7 g/cm³, which is a third of the density of steel [9–11,13]. Although Al alloys have a lower elastic modulus and yield strength than typical automotive steels, their low density gives them a comparable specific modulus (elastic modulus divided by density) and improved specific strength (yield strength divided by density) when compared to automotive steels, as seen in Table 1-1. As a result, a part made out of an Al alloy will need to be about 1.43 times thicker than an automotive steel part if designing to achieve equal bending stiffness, and 1.12 times thicker to achieve equal bending strength [9,12]. This results in a total weight decrease of 51% and 62%, respectively [12]. In addition, Al alloys offer improved extrusion properties compared to automotive steels, but have lower formability and cost 3-4 times more than steel [9].

Magnesium (Mg) alloys, on the other hand, have been used sparingly in automotive design, with most of their uses being in the interior of cars [9,14]. Mg alloys, with densities around 1.8 g/cm³, are the lightest structural metals [9–11,13]. As seen in Table 1-1, the elastic modulus and yield strength of Mg alloys is lower than both that of
Al alloys and automotive steel, but the specific modulus of Mg alloys is comparable to that of both steel and Al alloys. In addition, the specific strength of Mg alloys is greater than that of steel and Al alloys. As a result, an automotive part made out of a Mg alloy will need to be 1.67 times thicker than an automotive steel part when designing to achieve an equal bending stiffness, and 1.12 times thicker when designing for equal bending strength [9,12]. This results in a total weight decrease of 61% when designing for equal bending stiffness and 74% when designing for equal bending strength. Additionally, if Mg alloys were to be substituted in place of Al alloys, it would result in a 9% total weight decrease when designing to achieve an equal bending stiffness, and a 25% total weight decrease when designing for equal bending strength [12,15]. These potential weight savings have resulted in a stronger push by the automotive industry to introduce Mg alloys into automotive designs [12,14,15].

In addition to being lightweight, Mg alloys also have improved fluidity, machining, and vibration damping properties over Al alloys and steel [16–18]. However, Mg alloys currently have several limitations, including limited cold workability and toughness, limited strength and creep resistance above 120 degrees Celsius (°C), limited corrosion resistance, high chemical reactivity, and higher alloy cost compared to steel or Al alloys [9,14]. In particular, the limited strength and creep resistance above 120°C must be addressed, as car parts such as the powertrain reach temperatures above 120°C [9]. For commonly used Mg-based alloy series such as the Magnesium-Aluminum-Zinc (AZ) and the Magnesium-Aluminum-Manganese (AM) series, the limited strength and creep resistance above 120°C results from the discontinuous precipitation of the Mg₁₇Al₁₂
phase [19–21]. However, the Mg$_{17}$Al$_{12}$ precipitate acts as the primary strengthening phase for the AZ and AM series at room temperature.

The desire to improve creep resistance while maintaining Mg$_{17}$Al$_{12}$ as the primary strengthening phase in Mg alloys has led to the study of additional Mg-Al based ternary systems [22–24]. Studies have shown that the Magnesium-Aluminum-Silicon (AS) and Magnesium-Aluminum-Rare Earth (AE) series have improved creep resistance, but each series has its own limitations [22–24]. In particular, the AS series has poor corrosion resistance, and the AE series has high alloy cost due to the use of Rare Earth (RE) elements [22–24].

Due to the above limitations of Al-containing Mg alloys, current research has turned towards the development of Mg alloys without Al [25,26]. Studies have shown that Magnesium-Tin (Mg-Sn) alloys are a promising alternative because of their improved thermal stability over Mg-Al alloys. The improved thermal stability is attributed to the precipitation of the Mg$_2$Sn phase, which has a melting point of 770°C [27,28]. Additionally, Sn has a solubility of 14.5 weight percent (wt %) at the Mg-Sn eutectic temperature of 561°C and a room temperature solubility of less than 1 wt %, giving Mg-Sn alloys great potential to be precipitation hardened by Mg$_2$Sn [28,29]. However, the higher thermal stability achieved by Mg-Sn alloys comes with lower ductility and corrosion resistance [30]. Recent studies have shown that adding small amounts of silver (Ag) to Mg-Sn alloys can improve the ductility while still forming the desired Mg$_2$Sn precipitate [31,32]. However, the addition of Ag also resulted in the formation of Mg-Ag and Mg-Ag-Sn phases, some of which may be undesirable phases [31,32]. In
order to control the precipitates that form in the Mg-Ag-Sn system, the kinetics of the Mg-Ag-Sn system must first be understood.

In 2011, President Obama launched the Materials Genome Initiative, focused on developing advanced materials at a faster rate for a fraction of the current cost [33]. This has created a need to incorporate predictive models into the design process in order to lower the number of experiments needed and thereby speed up the design process and lower design cost [34]. One such example is the Calculation of Phase Diagrams (CALPHAD) approach to materials design, which focuses on using the experimental descriptions of lower alloy systems in conjunction with thermodynamic and kinetic databases to predict the thermodynamics and kinetics of higher order systems where limited experimental data exists [35,36].

There have been a significant number studies on Mg alloys to develop thermodynamic descriptions and implement this data into phase equilibria software such as FactSage, Pandat, and Thermo-Calc [37,38]. However, kinetic databases for Mg alloys remain underdeveloped. Recently, kinetic databases were developed for both Thermo-Calc and Pandat [39,40]. Of these, the only commercially available kinetic databases are in Thermo-Calc's diffusion module, Diffusion Controlled Transformations (DICTRA) [40,41]. However, much of the diffusion data of the binary systems, including Mg-Sn, were calculated from experiments using single crystals. Only one ternary system, Magnesium-Aluminum-Zinc (Mg-Al-Zn), has an experimental dataset from which atomic mobility values can be calculated [40]. This thesis focuses on the experimental calculation of diffusion coefficient values for polycrystalline Mg-Ag, Mg-Sn, and Mg-Ag-Sn systems. This experimental diffusion data was then optimized using the
DICTRA module of Thermo-Calc, and will be available commercially in Thermo-Calc's Mg-based alloy kinetic database for commercial alloy design.
<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>Elastic Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Specific Modulus (GPa•cm$^3$/g)</th>
<th>Specific Strength (MPa•cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanized Steel</td>
<td>7.8</td>
<td>210</td>
<td>200</td>
<td>26.9</td>
<td>25.6</td>
</tr>
<tr>
<td>5000 Series Al Alloy</td>
<td>2.7</td>
<td>71</td>
<td>159</td>
<td>26.3</td>
<td>58.9</td>
</tr>
<tr>
<td>AZ91 Mg Alloy</td>
<td>1.8</td>
<td>45</td>
<td>160</td>
<td>25.0</td>
<td>88.9</td>
</tr>
</tbody>
</table>
CHAPTER 2
LITERATURE REVIEW

Diffusion can be defined as the spontaneous mixing of atoms due to random thermal motion [42]. This thermal motion of atoms can be found in solids, liquids, and gases, and can be described as a flux of atoms passing through an area over a period of time [43]. This can be described by Fick’s First Law (Equation 2-1).

\[
J_i = -\bar{D}_i \frac{dC_i}{dx}
\]  

(2-1)

In Equation 2-1, \(J_i\) is the flux density of component \(i\), \(\bar{D}_i\) is the chemical diffusion coefficient, \(dC_i\) is the change in concentration of component \(i\), and \(dx\) is the change in distance [43]. It is important to note that Fick’s First Law makes a few assumptions about the solution in question. First, Fick’s First Law applies only to thermodynamically ideal solutions such as a Copper (Cu) and Nickel (Ni) solid solution [42]. Additionally, Fick’s First Law only applies in situations when the driving force for diffusion is small. Finally, Fick’s First Law assumes that the diffusion coefficient doesn’t change with composition.

In solids, there exist two common mechanisms by which atoms diffuse: vacancy and interstitial [42,44]. The mechanism by which an atom diffuses is dependent on the atomic size of the solvent in comparison to the atomic size of the solute it is diffusing through. For atoms that are a similar size as the atoms making up the lattice of the solid solution, the atoms diffuse by the vacancy mechanism. In order for atoms to diffuse using the vacancy mechanism, the neighboring lattice site of the diffusing atom should be vacant. Then, upon receiving the requisite amount of activation energy, the diffusing atom will jump from its current lattice site to the vacant lattice site, as seen in Figure 2-1.
The activation energy needed for this to take place is the sum of the energy for the atom to jump as well as the energy needed to form a vacancy [42].

For atoms that are much smaller in size than the atoms making up the lattice of the solid solution, the interstitial mechanism is the method by which they diffuse. This mechanism occurs by an atom moving in between lattice sites, as seen in Figure 2-2. As no activation energy is needed to create a vacancy for the atom to jump to, the activation energy needed for interstitial diffusion is typically less than that for vacancy diffusion [42].

Diffusion in the solid state is strongly dependent on temperature due to the high density of the solid state compared to liquid and gases. The higher density requires greater thermal energy for atoms to jump to a neighboring vacant site [42]. The temperature dependence of diffusion coefficients fits an Arrhenius model, as seen in Equation 2-2 [44].

\[
D = D_0 e^{-\frac{Q}{RT}}
\]  

In Equation 2-2, \(D\) is the diffusion coefficient, \(D_0\) is the pre-exponential factor, \(Q\) is the activation energy for diffusion, \(T\) is the temperature, and \(R\) is the universal gas constant. When the diffusion coefficient is plotted on a logarithmic (log) scale against the inverse of temperature, this produces a straight line from which the activation energy and pre-exponential factor can be calculated, as seen in Figure 2-3.

For a hexagonal close packed (HCP) Mg lattice, the majority of atoms diffuse using the vacancy mechanism. In the HCP Mg lattice, this mechanism can occur in two ways: the jumping of the diffusing atom to the nearest neighbor vacant site within the same basal plane (or a-axis), or the jumping of the diffusing atom from one basal plane
into the nearest neighbor vacant site in an adjacent basal plane (along the c-axis) [45]. This is illustrated in Figure 2-4. Since the Mg HCP lattice is 1.62 times longer in the c-axis than it is in the a-axis, the diffusion coefficients for the two methods of atomic jump in the Mg HCP lattice will be different [46]. Therefore, for single crystals, the diffusion coefficient will need to be calculated both perpendicular and parallel to the c-axis [45]. However, calculating the diffusion coefficient of a polycrystalline Mg alloy will have a variety of grain orientations, and therefore diffusion in both jump directions. As a result, calculating the diffusion coefficient of a polycrystalline Mg alloy can be used to determine an effective average diffusion coefficient of the two atomic jump directions [40].

In many practical applications, the solid solution in question is not thermodynamically ideal, the driving force for diffusion becomes very large, or the diffusion coefficient changes with composition. In such cases, Fick’s First Law no longer applies. For non-ideal solid solutions, the diffusion coefficient can be calculated by three methods: tracer diffusion, interdiffusion, and intrinsic diffusion [44]. Tracer diffusion is measured experimentally using radioactive isotopes [44]. While more difficult to obtain experimentally, diffusion coefficients calculated using tracer diffusion are independent of a thermodynamic factor. This eliminates having to use a thermodynamic database in conjunction with diffusion experiments, and any errors that would potentially arise from doing so. The tracer diffusion coefficient can be calculated using the Einstein Equation (Equation 2-3) [44].

\[ D_i^* = RTM_i \]  

(2-3)
In Equation 2-3, $D_i^*$ is the tracer diffusion coefficient of component $i$, $M_i$ is the atomic mobility of component $i$, $R$ is the universal gas constant, and $T$ is the temperature. In many cases, however, tracer diffusion experiments are not practical or possible.

A more practical way to measure diffusion coefficients is through diffusion couples, which consists of two dissimilar materials placed in contact with each other and heated to elevated temperatures to accelerate diffusion [42]. This method can be used to calculate the interdiffusion or intrinsic diffusion coefficient of each of the components of the diffusion couple [42,44]. The diffusion coefficient can be described using Fick’s Second Law (Equation 2-4) [43].

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial C_i}{\partial x} \right) \quad (2-4)$$

In Equation 2-4, $\partial C_i$ is the partial derivative of the concentration of component $i$, $\partial t$ is the partial derivative of time, $\partial x$ is the partial derivative of distance, and $D_i$ is the diffusion coefficient of component $i$. By assuming $D_i$ to be constant, Fick’s Second Law can be simplified to Equation 2-5 [44].

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad (2-5)$$

In Equation 2-5, $\partial^2 C_i$ is the second order partial derivative of the concentration of component $i$, and $\partial x^2$ is the partial derivative of the square distance.

Boltzmann further transformed Fick’s Second Law from a partial differential equation into an ordinary differential equation using a transformation variable (Equation 2-6) [47].

$$\eta = \frac{x}{\sqrt{t}} \quad (2-6)$$
In Equation 2-6, \( \eta \) is the Boltzmann transformation variable, \( x \) is the distance, and \( t \) is the time. Plugging this variable into Fick’s Second Law makes it possible to extract \( D_i \) from an experimentally observed concentration profile, such as in Figure 2-5, by using Equation 2-7 [47].

\[
-\frac{\eta}{2} \frac{dC_i}{d\eta} = \frac{d}{d\eta} \left( D_i \frac{dC_i}{d\eta} \right) \tag{2-7}
\]

In Equation 2-7, \( d\eta \) is the change in \( \eta \), and \( dC_i \) is the change in concentration of component \( i \).

It is important to note that Equation 2-7 is only useful if the initial conditions can be described in terms of \( \eta \). Matano applied Equation 2-7 to solve for \( D \) for diffusion couples with constant volume, also known as the volume fixed frame of reference [48]. Matano defined the initial conditions of the diffusion couple in terms of \( \eta \), resulting in Equation 2-8.

\[
D(C^*) = -\frac{1}{2t} \left( \frac{dx}{dc} \right)_{C=C^*} \int_{C^+}^{C^-} (x^* - x_0) dC \tag{2-8}
\]

In Equation 2-8, \( D(C^*) \) is the interdiffusion coefficient at concentration \( C^* \), \( C^* \) is the concentration at distance \( x^* \), \( C^{\pm \infty} \) is the concentration at the terminal ends of the diffusion couple, and \( x_0 \) is the Matano plane. In order for \( D(C^*) \) values calculated using Equation 2-8 to be accurate, the Matano plane must first be located. The location of the Matano plane, or the plane of mass balance indicated as \( x_0 \), is determined by Equation 2-9 [48,49]. An example of this can be seen in Figure 2-6.

\[
\int_{C^0}^{C^\infty} x dC + \int_{C^\infty}^{C^0} x dC = 0 \tag{2-9}
\]

In Equation 2-9, \( C \) is the concentration, \( C^{\pm \infty} \) is the concentration at the terminal ends of the diffusion couple, and \( C^0 \) is the concentration at the Matano plane. However, finding
the Matano plane is a time-consuming process with large amounts of error [50]. As previously stated, each of the components of a solid solution has their own unique diffusion coefficient [42,44]. As a result, in a diffusion couple with two dissimilar components on either side, the faster diffusing component will shift the boundary between the two components towards the side of the slower diffusion component, while leaving porosity behind on the side of the faster diffusing component [51,52]. This phenomenon is known as the Kirkendall Effect, and can make it difficult to find the point at which the mass of both sides of the diffusion couple is balanced. Additionally, the Matano plane may not lie at a point of experimental data collection.

Sauer, Friese, den Broeder, and Wagner modified Equation 2-9 so that the Matano plane no longer needed to be found in order to calculate $D_i(C^*)$ [53–55]. This resulted in Equation 2-10.

$$D(C^*) = \frac{1}{2t} \left( \frac{dx}{dC} \right)_{C=C^*} \left[ (1 - \psi) \int_{x^*}^{\infty} (C^* - C^\infty) \, dx + \psi \int_{-\infty}^{x^*} (C^\infty - C^*) \, dx \right]$$  \hspace{1cm} (2-10)

In Equation 2-10, $D(C^*)$ is the interdiffusion coefficient at concentration $C^*$, $t$ is the time, $dx$ is the change in distance at $C^*$, $dC$ is the change in concentration at $C^*$, $C^*$ is the concentration at distance $x$, $C^{\pm\infty}$ is the concentration at the terminal ends of the diffusion couple, and $\psi$ is a concentration ratio as defined in Equation 2-11.

$$\psi = \frac{C^* - C^\infty}{C^\infty - C^-\infty}$$  \hspace{1cm} (2-11)

Without having to find the Matano plane, the errors in calculating $D(C^*)$ using the Boltzmann-Matano method are greatly reduced [56].

While the Boltzmann-Matano method can measure diffusion in the volume fixed frame of reference, it cannot measure the rates of diffusion of individual components
relative to local lattice planes [57]. From Kirkendall’s diffusion couple experiments with brass, it was found that a net flux of atoms across any lattice plane exists, and the lattice plane shifts accordingly to conserve the density of lattice sites [52]. This shift of lattice planes is observed as a movement of inert markers placed on the diffusion couple [52]. This movement of markers can be measured by Equation 2-12 [52].

\[ v = \frac{x}{2t} \]  \hspace{1cm} (2-12)

In Equation 2-12, \( v \) is the Kirkendall (marker) velocity, \( x \) is the distance, and \( t \) is the time. If interdiffusion coefficient and Kirkendall velocity values are known from experiment for a binary system, the intrinsic diffusion coefficient in the lattice fixed frame of reference can be found using Darken’s Equation (Equation 2-13) [58].

\[ D = X_A D_B^I + X_B D_A^I \]  \hspace{1cm} (2-13)

In Equation 2-13, \( X_A \) is the mole fraction of component \( A \), \( D_B^I \) is the intrinsic diffusion of component \( B \), \( X_B \) is the mole fraction of component \( B \), and \( D_A^I \) is the intrinsic diffusion of component \( A \). The marker velocity can then be measured using Equation 2-14 [58].

\[ v = (D_A^I - D_B^I) \frac{\partial X_A}{\partial x} \]  \hspace{1cm} (2-14)

In Equation 2-14, \( \partial X_A \) is the partial derivative of the mole fraction of component \( A \).

Understanding the kinetics of an alloy system can assist in controlling the microstructure of the alloy. In particular, the diffusion coefficients of each component in an alloy have a significant effect on the coarsening rate of precipitates in the alloy, as seen in Lifshitz-Slyozov-Wagner (LSW) model (Equation 2-15) [59,60].

\[ (\bar{r})^3 - r_0^3 = \frac{8DV_mX_e t}{9RT} \]  \hspace{1cm} (2-15)

In Equation 2-15, \( (\bar{r})^3 \) is the average radius of all particles, \( r_0^3 \) is the radius at the onset of coarsening, \( D \) is the diffusion coefficient, \( \gamma \) is the interfacial free energy, \( V_m \) is the
molar volume of the precipitate, and \( X_e \) is the solubility. By understanding the diffusion coefficients of all the components in an alloy, the coarsening rate of precipitates in the alloy can be controlled, which in turn allows for properties such as strength, ductility, and creep resistance to be controlled.

To accelerate the process of materials design and to lower the cost of the materials design process, predictive modeling software is being integrated throughout the design process [34]. Three such programs that are currently used to model phase equilibria of materials systems are FactSage, Pandat, and Thermo-Calc [61–63]. All three programs utilize databases containing thermodynamic descriptions of elements and compounds to calculate phase diagrams, solidification models, and other thermodynamic properties of higher order systems that are experimentally unavailable [61–63]. In all three programs, the databases can be appended to experimental data from lower order systems that have been optimized using in-program optimization modules [61–63]. However, FactSage only has thermodynamic databases, and therefore does not have the capability to model the kinetics of material systems [61].

Both Pandat and Thermo-Calc, on the other hand, have thermodynamic and kinetic databases [62,63]. These kinetic databases, like their thermodynamic counterparts, can be appended to experimental data from lower order systems that have been optimized using in-program optimization modules [62,63]. However, a kinetic database developed using diffusion coefficient values would be impractical. Since most solid solutions are not thermodynamically ideal, the effect of composition of all the components of the solid solution must be taken into account. As a result, a kinetic database developed using diffusion coefficient values would require a separate diffusion
coefficient for every possible composition of solid solutions being examined. This would make the database overly complex. Therefore, atomic mobility values are stored in the kinetic database [64]. This relationship between the experimental diffusion coefficient and atomic mobility depends on the type of diffusion experiment used and the frame of reference [65].

The preferred type of experimental diffusion data for optimizing atomic mobility values is tracer diffusion (Equation 2-3), as it does not require data from a thermodynamic database [44,65]. This reduces the potential for error when calculating the atomic mobility values to store in the database. When tracer diffusion data cannot be obtained, interdiffusion data in the volume fixed frame of reference can be related to the atomic mobility assuming diffusion by the vacancy mechanism through Equation 2-16 [65].

\[
D_{k,j}^V = \Sigma_{i=1}^{i-1}(\delta_{ik} - X_k)X_iM_i\frac{\partial\mu_i}{\partial X_j}
\]  

Equation 2-16

In Equation 2-16, \(D_{k,j}^V\) is the volume fixed frame of reference diffusion coefficient, \(\delta_{ik}\) is the Kronecker delta function, \(X_k\) is the mole fraction of component \(k\), \(X_i\) is the mole fraction of component \(i\), \(\partial\mu_i\) is the partial derivative of the chemical potential of component \(i\), and \(\partial X_j\) is the partial derivative of the mole fraction of component \(j\). Unlike tracer diffusion, interdiffusion coefficients require input from a thermodynamic database, and therefore are dependent on the accuracy of the thermodynamic database [65]. Finally, intrinsic diffusion data in the lattice fixed frame of reference can be related to the atomic mobility assuming diffusion by the vacancy mechanism through Equation 2-17 [65].
\[ D_{kj}^L = \sum_i M_{ki} \frac{\partial \mu_i}{\partial X_j} \]  

(2-17)

In Equation 2-17, \( D_{kj}^L \) is the lattice fixed frame of reference diffusion coefficient, and \( M_{ki} \) is the atomic mobility of component \( i \) in gradient \( k \). Like with interdiffusion coefficients, intrinsic diffusion coefficients require input from a thermodynamic database [65].

In these atomic mobility matrices utilized by both programs, only the diagonal atomic mobility terms are modeled, and the off-diagonal terms are assumed to be equal to zero [65]. This assumption is reasonable because the atomic jump correlation effects that are associated with off-diagonal atomic mobility terms are almost indistinguishable from experimental data scatter [64]. With this in mind, the kinetic databases used by Thermo-Calc and Pandat solve for atomic mobility using Equation 2-18 [65].

\[ M_i = M_i^0 \frac{1}{RT} \exp \left( -\frac{Q_i}{RT} \right) \]  

(2-18)

In Equation 2-18, \( M_i^0 \) is the atomic mobility frequency factor, and \( Q_i \) is the activation energy for diffusion of component \( i \). When there is no magnetic effect on \( M_i \), \( M_i^0 \) is set to one, and only the composition and temperature effects on \( M_i \) are considered [65].

Following the CALPHAD approach to thermodynamic free energy modeling, the effect of composition on the activation energy can be determined using the Redlich-Kister polynomial (Equation 2-19) [35,65,66].

\[ Q_i = \sum_j X_j Q_i^j + \sum_p \sum_{j>p} X_p X_j \sum_k A_i^{pj}(X_p - X_j)^k \]  

(2-19)

In Equation 2-19, \( Q_i^j \) is the activation energy for diffusion of component \( i \) in pure component \( j \), \( X_j \) is the mole fraction of component \( j \), \( X_p \) is the mole fraction of component \( p \), and \( A_i^{pj} \) is an interaction parameter. Although studies have been done on Mg alloys using both Pandat’s and Thermo-Calc’s diffusion modules, only Thermo-Calc
has a commercially available kinetic database for Mg alloys [39–41]. As a result, Thermo-Calc and its corresponding kinetic modeling software, DICTRA, were utilized in this study.

Diffusion in the Mg-Ag system has been investigated by two experimental studies and three computational studies [40,67–70]. Lal studied tracer diffusion of $^{110}$Ag in polycrystalline Mg in the temperature range of 476.5–621°C [67]. The samples were sectioned using a precision lathe and their activity measured using a scintillator [67]. Combronde, on the other hand, studied tracer diffusion of $^{110}$Ag in single crystal Mg in the temperature range of 479–639°C [68]. This was done by abrading fixed amounts of materials and measuring the activity penetration curves [68]. Recently, Bryan optimized the experimental data of Lal and Combronde using DICTRA’s Parrot optimizing software, and added the resulting optimized atomic mobility parameter values to DICTRA’s kinetic database [40]. Finally, both Wu and Zhou calculated the diffusion of Ag in single crystal Mg using first-principles Density Function Theory (DFT) in the Vienna Ab-Initio Simulation Package (VASP) [69,70]. The diffusion coefficients of all the studies are plotted in Figure 2-7 and are discussed below.

Diffusion of Ag in Mg has been thoroughly studied, with experimental data sets for both single crystal and polycrystalline diffusion, and multiple computational studies. However, there is a wide variety of results between the experimental and computational studies. The single-crystal experimental study done by Combronde showed that diffusion coefficient values were 1.56-2.37 times larger parallel to the c-axis than perpendicular to the c-axis [68]. On the other hand, Wu’s VASP model had larger diffusion coefficient values perpendicular to the c-axis than parallel to the c-axis, while
achieving similar diffusion coefficient values as those determined experimentally by Combronde [69]. Similarly, Zhou’s VASP model had larger diffusion coefficient values perpendicular to the c-axis than parallel to the c-axis [70]. However, Zhou’s VASP model produced diffusion coefficient values that are much lower than found experimentally by Combronde or Lal [70]. Lal’s work with polycrystalline Mg produced diffusion coefficient values that lie in between Combronde’s parallel and perpendicular single-crystal values [67]. Bryan’s use of Combronde’s and Lal’s datasets to optimize the atomic mobility parameters in DICTRA led to diffusion coefficient values that sit between Combronde’s and Lal’s experimental data, representing an effective average diffusion coefficient [40].

Diffusion in the Mg-Sn system has been investigated by one experimental study and four computational studies [40,68–71]. Combronde studied tracer diffusion of $^{113}$Sn in single-crystal Mg in the temperature range of 475-629°C [68]. Concentration profiles were determined by radioactivity measurements of cuttings made with a precision lathe [68]. However, the diffusion coefficient was only measured at two different temperatures perpendicular to the c-axis compared to four different temperatures parallel to the c-axis [68]. Bryan optimized Combronde’s experimental data using DICTRA’s Parrot optimizing software, and added the resulting optimized atomic mobility parameter values to DICTRA’s kinetic database [40]. Finally, Ganeshan, Wu, and Zhou calculated the diffusion of Sn in single crystal Mg using first-principles DFT in VASP [69–71]. The diffusion coefficients of all the studies are plotted in Figure 2-8 and are discussed below.

Diffusion of Sn in Mg has been insufficiently studied experimentally, but has multiple computational studies. Although Combronde’s two experimental diffusion
coefficient measurements perpendicular to the c-axis are similar in value to diffusion coefficient measurements parallel to the c-axis at the same temperature, more experimental data points would be needed to show whether there is a significant difference between the two atomic jump directions for Sn in Mg [68]. As a result, Bryan's diffusion coefficient values were almost identical to Combronde's experimental diffusion coefficient measurements parallel to the c-axis [40]. Using VASP models, Ganeshan, Wu and Zhou were able to calculate diffusion coefficient values both parallel and perpendicular to the c-axis [69,70]. Ganeshan's diffusion coefficient values were slightly larger parallel to the c-axis than perpendicular to the c-axis [71]. However, Ganeshan's VASP model produced diffusion coefficient values that are much lower than those calculated experimentally by Combronde [71]. Wu's diffusion coefficient values, on the other hand, are larger perpendicular to the c-axis than parallel to the c-axis [69]. Additionally, Wu's diffusion coefficient values more closely match those determined experimentally by Combronde. Likewise, Zhou's diffusion coefficient values are larger perpendicular to the c-axis than parallel to the c-axis, and are similar to the values determined experimentally by Combronde [70].

Diffusion in the Mg-Ag-Sn system has currently not been investigated by any studies in literature. Additionally, in the commercially available MGMOB1 database, there exists only one ternary system, the Mg-Al-Zn system, as seen in Figure 2-9 [40,67,68,72–74]. This necessitates the kinetic study of additional Mg-based ternary systems so that kinetic descriptions of these systems will be commercially available in databases for materials development and design.
Figure 2-1. Schematic of vacancy diffusion mechanism.
Figure 2-2. Schematic of interstitial diffusion mechanism.
Figure 2-3. Temperature dependence of the diffusion coefficient in solids, as described by the Arrhenius relationship. In Figure 2-3, the x-axis is the inverse of temperature in Kelvin (K).
Figure 2-4. Schematic of an HCP lattice with the two possible atomic jump directions highlighted with blue lines. In Figure 2-4, the red lines indicate the a-axis and c-axis.
Figure 2-5. Example of a concentration profile extracted from a diffusion couple.
Figure 2-6. Example of a Matano plane.
Figure 2-7. Data from literature of the diffusion coefficient of Ag in Mg [40,67–70]. In the legend of Figure 2-7, Perp represents diffusion perpendicular to the c-axis, Para represents diffusion parallel to the c-axis, and PX represents diffusion in polycrystalline Mg.
Figure 2-8. Data from literature of the diffusion coefficient of Sn in Mg [40,68–71]. In the legend of Figure 2-8, Perp represents diffusion perpendicular to the c-axis, Para represents diffusion parallel to the c-axis, and PX represents diffusion in polycrystalline Mg.
Figure 2-9. Temperature-dependent diffusion coefficients of all relevant solutes in Mg, as found in the MGMOB1 atomic mobility database [40, 67, 68, 72–74].
CHAPTER 3
MATERIALS AND METHODS

All Mg alloys were cast using a resistive furnace built into an argon (Ar) backfilled glove box. Magnesium granules (99.8% purity), Sn shot (99.8% purity), and Ag powder (99.95% purity) were used as initial materials. The raw materials were weighed to the desired composition and placed into a graphite crucible coated with boron nitride. The boron nitride coating on the crucible was used to minimize sticking after casting. The crucibles were then placed into the resistive furnace in the glove box at 750°C and covered with a graphite lid. To prevent the highly exothermic reaction of molten Mg with oxygen gas (O₂), the O₂ level in the glove box was maintained at a concentration less than 100 parts per million (ppm).

A Mg-Ag master alloy was prepared by melting Mg and Ag for 1 hour. While in the furnace, the molten metal was stirred twice using a graphite rod coated in boron nitride. This was then cast into a 60 gram (g) rectangular mold coated in boron nitride, and allowed to air cool. The composition of the alloy was verified with energy dispersive x-ray spectroscopy (EDS) in a TESCAN MIRA3 scanning electron microscope (SEM), and can be seen in Table 3-1. The remaining alloys were prepared by melting Mg, Sn, and the Mg-Ag master alloy for 25 minutes. At the 20-minute point, the molten alloys were stirred while still in the furnace using a graphite rod coated in boron nitride. After 25 minutes, the alloys were cast into a 60-g rectangular mold coated in boron nitride and allowed to air cool. The composition of each alloy was verified using wavelength dispersive spectroscopy (WDS) in a CAMECA SXFiveFE electron probe microanalyzer (EMPA), and can be seen in Table 3-1.
To ensure that all alloys were a single phase, each of the alloys went through a solutionizing heat treatment step after casting. To prepare the alloys for heat treatment, each was cut into four approximately equal sections using a silicon carbide (SiC) abrasive saw. Each section was then placed into 1-inch diameter Pyrex tubes and evacuated to less than 40 millitorr (mTorr) and purged with Ar three times. After the final purge, the section was then encapsulated in the Pyrex tube using a hydrogen-oxygen torch. The encapsulated samples were then heat treated in an open-air resistive furnace at 450°C for 24 hours.

Rectangular sections of each solutionized alloy were cut into sections approximately 5 millimeters (mm) wide, 10 mm long, and 3 mm thick using a low-speed diamond saw. The surfaces of each section that were going to be in contact in the diffusion couple were ground and polished to 1 micrometer (μm) using a series of SiC abrasive papers and a cloth polishing pad. A summary of all the steps in this process can be seen in Table 3-2. After completion of the 600-grit SiC planing step, each sample was attached to a lapping fixture using Crystalbond adhesive. The lapping fixture was used to ensure that all sides of each sample were completely flat. After completion of the 1 μm polishing step, each sample was removed from the lapping fixture and residual Crystalbond was removed using acetone.

The polished surfaces of both ends of the diffusion couple were then placed in contact with each other and the diffusion couple was wrapped in tantalum (Ta) foil. The Ta foil was used as an oxygen getter to limit Mg alloy oxidation. The diffusion couple was then placed in a Kovar jig and tightened with a torque wrench such that the pressure on the bolts was 5 ft-lbs. Assembled diffusion couples with the jig were then
encapsulated in Pyrex tubes under a vacuum below 40 mTorr using a hydrogen-oxygen torch. An example of an encapsulated diffusion couple jig can be seen in Figure 3-1. All diffusion couples were annealed in an open air resistive furnace. The temperature of the furnace was verified daily using a thermocouple. The ends of each diffusion couple, along with annealing time and temperature, can be seen in Table 3-3. The annealing temperatures were chosen to ensure that the combination of temperature and composition was in the single-phase $\alpha$-Mg region, as well as to avoid any liquid regions of the phase diagram. The phase diagrams for all of the alloys used can be seen in Appendix A. Additionally, the annealing times were selected so that each diffusion couple would have diffusion through the initial interface between the two metals.

After the heat treatment was completed, each diffusion couple was water-quenched to stop diffusion. Each was then rinsed in ethanol and mounted in 1-inch diameter acrylic mounts. The mounts were then sectioned in half perpendicular to the diffusion interface, and each half was remounted in acrylic. A schematic of this sectioning process can be seen in Figure 3-2. Each mounted sample was ground and polished to 1 $\mu$m using the steps in Table 3-2. As the acrylic mount was already flat on both sides, the lapping fixture was not needed for polishing. Each mounted and polished diffusion couple was then placed in a vacuum box to degas the acrylic mount for at least 12 hours. After degassing, the diffusion couples were analyzed using EPMA-WDS. Element calibrations were performed with pure element standards, and a diffusion profile line scan was performed perpendicular to the diffusion interface. The length of the line scan and the step size between points for each diffusion couple was chosen so that there would be at least 100 points on each end that were outside the diffusion zone.
This was done so that there would be enough points on either end of the concentration profile to accurately determine the values of \( C^\infty \) and \( C^{*-\infty} \) for Equation 2-10 and Equation 2-11. Each diffusion couple and its corresponding line scan length and step size can be seen in Table 3-4.

Each concentration profile was smoothed using a cubic b-spline interpolation function in Origin Graphing and Data Analysis Software (Origin) [75]. This was done to reduce the data scatter when calculating \( D(C^*) \), and to achieve a more precise calculation of the diffusion profile integrals as well as the differential found in Equation 2-10. An example of this can be seen in Figure 3-3. The number of points in the cubic b-spline function was set to equal the number of points in the original concentration profile, and the smoothing factor varied between 5-10, depending on the number of points, length of the line scan, and the original composition. To verify the accuracy of the cubic b-spline to the original concentration profile, a coefficient of determination (\( R^2 \)) was calculated for each concentration profile and corresponding smoothed profile. The smoothing factor used and the resulting \( R^2 \) values for each concentration profile can be found in Table 3-5. The concentration-dependent interdiffusion coefficient of each diffusion couple was extracted from each concentration profile in Origin using Equation 2-10 and Equation 2-11. This data was then sorted by diffusion couple composition and put into experimental data files for use in DICTRA.

Thermo-Calc’s TCMG4 thermodynamic database was used in conjunction with the interdiffusion experimental data for the Mg-Sn, Mg-Ag, and Mg-Ag-Sn systems calculated using Equation 2-10 and Equation 2-11. The experimental interdiffusion coefficient data was optimized using the Parrot optimization module of DICTRA, which
yielded optimized atomic mobility parameters. This was done using a least-squares method in which the atomic mobility parameters were iteratively rescaled and optimized until the sum of squares difference between the experimental data input and the simulation was minimized. Simulations of the concentration-dependent interdiffusion coefficients and concentration profiles were then performed using DICTRA under the same time, temperature, and composition parameters as used for the original diffusion couple experiments. These were then compared to their experimental counterparts to determine the accuracy of the optimized atomic mobility values.

These optimized atomic mobility parameters were validated using independent diffusion couples that used different end members, annealing times, and annealing temperatures than were used in the atomic mobility optimization. The diffusion couple ends, annealing times and temperatures, and the atomic mobility parameters validated by each of these diffusion couples can be seen in Table 3-6. These validation diffusion couples were sectioned, ground, and polished using the same steps as used before in Figure 3-2 and Table 3-2. Each validation diffusion couple was degassed and analyzed with EPMA-WDS using the same techniques as used for the original diffusion couples. Each validation diffusion couple and its corresponding line scan length and step size can be found in Table 3-7. Each validation concentration profile was then compared to DICTRA simulations calculated under the same time, temperature, and composition parameters as the validation diffusion couples to validate the atomic mobility values.
### Table 3-1. Compositions of cast Mg alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Wt% Ag, Actual</th>
<th>Wt% Sn, Actual</th>
<th>Wt % Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Ag Master Alloy</td>
<td>44.30</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-5Ag</td>
<td>5.72</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-5Sn</td>
<td>-</td>
<td>5.90</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-2Ag</td>
<td>2.67</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-2Sn</td>
<td>-</td>
<td>2.25</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-2Ag-5Sn</td>
<td>2.53</td>
<td>5.59</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg-2Sn-5Ag</td>
<td>6.13</td>
<td>2.39</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### Table 3-2. Grinding and polishing steps for Mg alloys.

<table>
<thead>
<tr>
<th>Pad Type</th>
<th>Suspension</th>
<th>Polishing Time</th>
<th>Cleaning Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>120-grit SiC paper</td>
<td>Sink water</td>
<td>Until plane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>320-grit SiC paper</td>
<td>Sink water</td>
<td>Until plane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>600-grit SiC paper</td>
<td>Sink water</td>
<td>Until plane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>800-grit SiC paper</td>
<td>Sink water</td>
<td>Until plane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>1200-grit SiC paper</td>
<td>Sink water</td>
<td>Until plane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>1 μm polishing cloth</td>
<td>1 μm Alumina (Al₂O₃)</td>
<td>15 seconds</td>
<td>Deionized water cotton swab, Ethanol cotton swab</td>
</tr>
</tbody>
</table>

### Table 3-3. Diffusion couple heat treatments.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Mg-5Ag</td>
<td>450</td>
<td>24</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>500</td>
<td>24</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>550</td>
<td>24</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>450</td>
<td>48</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>500</td>
<td>24</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>550</td>
<td>24</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>450</td>
<td>192</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>500</td>
<td>24</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>550</td>
<td>24</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>450</td>
<td>48</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>500</td>
<td>24</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>550</td>
<td>24</td>
</tr>
</tbody>
</table>
Table 3-4. Diffusion couple line scan length and step size.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Anneal Temperature (°C)</th>
<th>Line Scan Length (μm)</th>
<th>Step Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Mg-5Ag</td>
<td>450</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>500</td>
<td>1339</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>550</td>
<td>2000</td>
<td>2</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>450</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>500</td>
<td>989</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>550</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>450</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>500</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>550</td>
<td>1500</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>450</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>500</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>550</td>
<td>3000</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3-5. Smoothing factor and R² values of each diffusion couple's concentration profile.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Anneal Temperature (°C)</th>
<th>Smoothing Factor</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Mg-5Ag</td>
<td>450</td>
<td>9</td>
<td>0.943</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>500</td>
<td>10</td>
<td>0.988</td>
</tr>
<tr>
<td>Mg/Mg-5Ag</td>
<td>550</td>
<td>7</td>
<td>0.993</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>450</td>
<td>6</td>
<td>0.975</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>500</td>
<td>7</td>
<td>0.989</td>
</tr>
<tr>
<td>Mg/Mg-5Sn</td>
<td>550</td>
<td>7</td>
<td>0.992</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>450</td>
<td>7</td>
<td>0.979</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>500</td>
<td>5</td>
<td>0.994</td>
</tr>
<tr>
<td>Mg-2Ag/Mg-2Ag-5Sn</td>
<td>550</td>
<td>8</td>
<td>0.995</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>450</td>
<td>8</td>
<td>0.989</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>500</td>
<td>7</td>
<td>0.993</td>
</tr>
<tr>
<td>Mg-2Sn/Mg-2Sn-5Ag</td>
<td>550</td>
<td>7</td>
<td>0.990</td>
</tr>
</tbody>
</table>

Note: Diffusion couples with Mg as an end member used 99.95% purity Mg rod.

Table 3-6. Validation diffusion couple heat treatments.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Anneal Temperature (°C)</th>
<th>Anneal Time (hours)</th>
<th>Mobility Parameter Verified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Mg-2Ag</td>
<td>525</td>
<td>18</td>
<td>$Q_{Ag}^{Mg}$, $v_{Ag}^{Mg,Ag}$</td>
</tr>
<tr>
<td>Mg/Mg-2Sn</td>
<td>525</td>
<td>18</td>
<td>$Q_{Sn}^{Mg}$, $v_{Ag}^{Mg,Sn}$</td>
</tr>
<tr>
<td>Mg/Mg-2Sn-5Ag</td>
<td>525</td>
<td>18</td>
<td>$v_{Ag}^{Mg,Sn}$</td>
</tr>
<tr>
<td>Mg/Mg-2Ag-5Sn</td>
<td>525</td>
<td>18</td>
<td>$v_{Ag}^{Mg,Ag}$</td>
</tr>
</tbody>
</table>
Table 3-7. Validation diffusion couple line scan length and step size.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Line Scan Length (µm)</th>
<th>Step Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Mg-2Ag</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-2Sn</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-2Sn-5Ag</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Mg/Mg-2Ag-5Sn</td>
<td>1000</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 3-1. An encapsulated diffusion couple jig.

Figure 3-2. Schematic of diffusion couple sectioning for EPMA-WDS.
Figure 3-3. Example of cubic b-spline concentration profile curve fitting in Origin.
CHAPTER 4
RESULTS AND DISCUSSION

All of the concentration profiles used in this study and the cubic b-spline interpolation curves fitted to each can be seen in Appendix B. The cubic b-spline interpolation function was used as it allows for a more precise calculation of the diffusion profile integrals as well as the differential found in Equation 2-10, which are critical to accurately assess the concentration-dependent interdiffusion coefficient [76]. The accuracy of each of the cubic b-spline curve fits of all the diffusion zones was found to be good, with 0.943 being the lowest $R^2$ value, as seen in Table 3-5. The interdiffusion coefficient was calculated using the modification of the Boltzmann-Matano method first used by Sauer, Friese, den Broeder, and Wagner, better known as the Sauer-Friese-den Broeder Method (Equation 2-10, Equation 2-11) [53–55]. This method was utilized as opposed to the Boltzmann-Matano method (Equation 2-8) as it eliminates the errors associated with finding the Matano plane, such as the Matano plane not lying on an experimentally observed point on the concentration profile (Equation 2-9) [56]. The concentration-dependent interdiffusion coefficients of Ag in Mg, Sn in Mg, Ag in Mg-Sn, and Sn in Mg-Ag can be found in Appendix C. Because of errors associated with the Sauer-Friese-den Broeder Method from calculations near the ends of the concentration profile, the concentration dependent interdiffusion coefficients are displayed from 1-4 wt %, instead of 0-5 wt %.

The first system assessed was the Mg-Ag binary system. Two mobility parameters were used to fit the experimental diffusion data of Ag in Mg. The primary mobility parameter for Ag in Mg is $Q_{Ag}^{Mg}$, while a secondary interaction parameter, $\Delta^{Ag,Mg}_{Ag}$, is used to improve fit by introducing a mobility term which evaluates the effect
of Ag concentration on Ag diffusion in Mg. The optimized atomic mobility values for Ag diffusion in Mg can be found in Table 4-1. These optimized atomic mobility parameters were then used to model the concentration-dependent interdiffusion coefficient of Ag in Mg in DICTRA. A comparison of the concentration-dependent interdiffusion coefficients produced by the DICTRA simulations and the corresponding experimental data can be seen in Figure 4-1. It can be observed that there is good correlation between the DICTRA simulations and the experimentally observed concentration-dependent interdiffusion coefficients. This can be attributed to the addition of the interaction parameter, which helped to improve the fit of the DICTRA simulations to the experimentally observed data. The experimentally observed concentration profiles for the Mg/Mg-5Ag diffusion couples as well as the corresponding DICTRA concentration profile simulations can be seen in Appendix D. It can be observed that there is good correlation between the experimentally observed concentration profiles and the DICTRA concentration profile simulations.

With confirmed correlation back to the experimentally observed concentration-dependent interdiffusion coefficients, the optimized atomic mobility parameters for Ag in Mg can now be used to simulate the temperature-dependent diffusion coefficient for Ag in Mg. These results, along with any previous literature data, can be seen in Figure 4-2. In Figure 4-2, it can be observed that the temperature-dependent diffusion coefficients calculated in this study correlates well to previous experimental studies done by Combronde and Lal [67,68]. This helps confirm the accuracy of the atomic mobility parameters calculated in this study, as Lal’s tracer diffusion studies were done with
polycrystalline Mg [67]. Additionally, Combronde’s tracer diffusion studies measured the diffusion of Ag in both atomic jump directions in Mg [68].

To validate the atomic mobility parameters of Ag in Mg, a diffusion couple was created with different end members, anneal time, and anneal temperature than the initial Ag in Mg diffusion experiments used to calculate the atomic mobility parameters. The resulting experimentally observed concentration profile was compared to a DICTRA simulation run with the same parameters, as seen in Figure 4-3. It can be observed that the DICTRA simulation correlates well to the experimentally observed concentration profile. This confirms the accuracy of the Ag in Mg mobility parameters, and shows that the $^{0}A_{Ag}^{Mg}$ interaction parameter was successful in improving the fit of the DICTRA simulations to the experimentally observed diffusion data.

Next, diffusion in the Mg-Sn binary system was assessed. Two mobility parameters were used to fit the experimental diffusion data of Sn in Mg. The principal mobility parameter for Sn in Mg is $Q_{Sn}^{Mg}$, while a secondary interaction parameter, $^{0}A_{Sn}^{Mg}$, is used to improve fit by introducing a mobility term which evaluates the effect of Sn concentration on Sn diffusion in Mg. The optimized atomic mobility values for Sn diffusion in Mg can be found in Table 4-1. These optimized atomic mobility parameters were then used to model the concentration-dependent interdiffusion coefficient of Sn in Mg in DICTRA. A comparison of the concentration-dependent interdiffusion coefficients produced by the DICTRA simulations and the corresponding experimental data can be seen in Figure 4-4. It can be observed that there is good correlation between the DICTRA simulations and the experimentally observed concentration-dependent interdiffusion coefficients. This can be attributed to the $^{0}A_{Sn}^{Mg}$ interaction parameter,
which helped to improve the fit of the DICTRA simulations to the experimentally observed data. The experimentally observed concentration profiles for the Mg/Mg-5Sn diffusion couples as well as the corresponding DICTRA concentration profile simulations can be seen in Appendix D. It can be observed that there is good correlation between the experimental and the DICTRA simulation concentration profiles.

With confirmed correlation back to the experimentally observed concentration-dependent interdiffusion coefficients, the optimized atomic mobility parameters for Sn in Mg can now be used to simulate the temperature-dependent diffusion coefficient for Sn in Mg. These results, along with results of previous studies, can be seen in Figure 4-5. It can be observed that the temperature-dependent diffusion coefficients calculated in this study differ significantly from the temperature-dependent diffusion coefficients determined by Combronde [68]. In particular, the temperature-dependent diffusion coefficient line generated in this study appears to have a lower activation energy than the temperature-dependent diffusion coefficient data determined by Combronde. This could be attributed to the fact that Combronde’s tracer diffusion studies were performed on single-crystal Mg. On the other hand, the current study calculates temperature-dependent diffusion coefficients for the diffusion of Sn in polycrystalline Mg, which is desired for materials design applications. Additionally, Combronde’s studies calculated the diffusion coefficient at only two different temperatures in the jump direction perpendicular to the c-axis as compared to four different temperatures parallel to the c-axis. Therefore, the effect diffusion perpendicular to the c-axis on the diffusion coefficient is unclear [68].
To validate the atomic mobility parameters of Sn in Mg, a diffusion couple was created with different end members, anneal time, and anneal temperature than the initial Sn in Mg diffusion experiments used to calculate the atomic mobility parameters. The resulting experimentally observed concentration profile was compared to a DICTRA simulation run with the same parameters, as seen in Figure 4-6. It can be observed that the DICTRA simulation correlates well to the experimentally observed concentration profile. This confirms the accuracy of the Sn in Mg mobility parameters, and shows that the $A_{Sn,Mg}^{Sn}$ interaction parameter was successful in improving the fit of the DICTRA simulations to the experimentally observed diffusion data.

With diffusion in both the Mg-Ag and Mg-Sn systems assessed, diffusion in the Mg-Ag-Sn ternary system was then assessed. One mobility parameter, $A_{Ag}^{Sn,Mg}$, was used to fit the experimental diffusion data of Ag in Mg-Sn, as the other mobility parameters, $Q_{Ag}^{Mg}$ and $A_{Ag}^{Ag,Mg}$, were already evaluated and optimized. The optimized atomic mobility parameter for Ag diffusion in Mg-Sn can be found in Table 4-1. These optimized atomic mobility parameters were then used to model the concentration-dependent interdiffusion coefficient of Ag in Mg-Sn in DICTRA. A comparison of the concentration-dependent interdiffusion coefficients produced by the DICTRA simulations and the corresponding experimental data can be seen in Figure 4-7. It can be observed that there is generally good correlation between the DICTRA simulations and the experimentally observed concentration-dependent interdiffusion coefficients. However, there are some discrepancies between the DICTRA simulations and the experimentally observed concentration-dependent interdiffusion coefficients, especially at 500°C for concentrations of Ag between 1-2 wt %. This could be due to the use of...
only one atomic mobility parameter, \( A_{Ag}^{Sn,Mg} \), to fit the experimental data. Using one atomic mobility parameter instead of multiple parameters lowers the fit accuracy. However, with the other atomic mobility parameters for Ag diffusion in Mg, \( Q_{Ag}^{Mg} \) and \( A_{Ag}^{Ag,Mg} \), already evaluated and optimized, only \( A_{Ag}^{Sn,Mg} \) needed to be optimized.

Additionally, the experimentally observed concentration profiles for the Mg-2Sn/Mg-2Sn-5Ag system as well as the corresponding DICTRA concentration profile simulations can be seen in Appendix D. It can be observed that there is good correlation between the experimentally observed concentration profiles and the DICTRA simulations.

With confirmed correlation back to the experimentally observed concentration-dependent interdiffusion coefficients, the optimized atomic mobility parameter for Ag in Mg-Sn can be used to simulate the temperature-dependent diffusion coefficient for Ag in Mg-Sn. To understand the effect of Sn on Ag diffusion in Mg, the temperature-dependent diffusion coefficient of Ag in Mg-Sn can be compared to the temperature-dependent diffusion coefficient of Ag in Mg, as seen in Figure 4-8. It can be observed that the addition of Sn decreases the activation energy needed for Ag diffusion in Mg. As a result, for temperatures below 550°C, the presence of Sn increases the diffusion rate of Ag in Mg.

To validate the atomic mobility parameter of Ag in Mg-Sn, a diffusion couple was created with different end members, anneal time, and anneal temperature than the initial Ag in Mg-Sn diffusion experiments used to calculate the atomic mobility parameters. The resulting experimentally observed concentration profile was compared to a DICTRA simulation run with the same parameters, as seen in Figure 4-9. It can be observed in Figure 4-9 that the DICTRA simulation correlates well to the experimentally
observed concentration profile, confirming the accuracy of the Ag in Mg-Sn atomic mobility parameter $^{0}A_{Ag}^{Sn,Mg}$.

One mobility parameter, $^{0}A_{Sn}^{Ag,Mg}$, was used to fit the experimental diffusion data of Sn in Mg-Ag, as the other mobility parameters, $Q_{Sn}^{Mg}$ and $^{0}A_{Sn}^{Sn,Mg}$, were already evaluated and optimized. The optimized atomic mobility parameter for Sn diffusion in Mg-Ag can be found in Table 4-1. The optimized atomic mobilities were then used to model the concentration-dependent interdiffusion coefficient of Sn in Mg-Ag in DICTRA. A comparison of the concentration-dependent interdiffusion coefficients produced by the DICTRA simulations and the corresponding experimental data can be seen in Figure 4-10. It can be observed that there is generally good correlation between the DICTRA simulations and the experimentally observed concentration-dependent interdiffusion coefficients. However, there are some discrepancies between the DICTRA simulations and the experimental data, especially at 500°C for concentrations of Sn between 3-4 wt %. This could be due to the use of only one atomic mobility parameter, $^{0}A_{Sn}^{Ag,Mg}$, to fit the experimental data. Using one atomic mobility parameter instead of multiple parameters lowers the fit accuracy. However, with the other atomic mobility parameters for Sn diffusion in Mg, $Q_{Sn}^{Mg}$ and $^{0}A_{Sn}^{Sn,Mg}$, already evaluated and optimized, only $^{0}A_{Sn}^{Ag,Mg}$ needed to be optimized. Additionally, the experimentally observed concentration profiles for the Mg-2Ag/Mg-2Ag-5Sn diffusion couples as well as the corresponding DICTRA concentration profile simulations can be seen in Appendix D. It can be observed that there is good correlation between the experimentally observed concentration profiles and the DICTRA simulations.
With confirmed correlation back to the experimentally observed concentration-dependent interdiffusion coefficients, the optimized atomic mobility parameters for Sn in Mg-Ag can be used to simulate the temperature-dependent diffusion coefficient for Sn in Mg-Ag. To understand the effect of Ag on Sn diffusion in Mg, the temperature-dependent diffusion coefficient of Sn in Mg-Ag can be compared to the temperature-dependent diffusion coefficient of Sn in Mg, as seen in Figure 4-11. It can be observed that the addition of Ag increases the activation energy needed for Sn diffusion in Mg. As a result, for temperatures below 500°C, the presence of Ag decreases the diffusion rate of Sn in Mg. With slower kinetics, the coarsening kinetics of precipitates can be better controlled, as seen in Equation 2-15. Controlling coarsening rates, in turn, can improve elevated temperature mechanical properties and creep resistance.

To validate the atomic mobility parameter of Sn in Mg-Ag, a diffusion couple was created with different end members, anneal time, and anneal temperature than the initial Sn in Mg-Ag diffusion experiments used to calculate the atomic mobility parameters. The resulting experimentally observed concentration profile was compared to a DICTRA simulation run with the same parameters, as seen in Figure 4-12. It can be observed that the DICTRA simulation correlates well to the experimentally observed concentration profile, confirming the accuracy of the Sn in Mg-Ag atomic mobility parameter \( A_{Sn}^{Ag,Mg} \).
Table 4-1. Optimized atomic mobility parameters used in DICTRA simulations.

<table>
<thead>
<tr>
<th>DICTRA Notation</th>
<th>Mobility Parameter</th>
<th>Value (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag diffusion</td>
<td>$Q_{Ag}^{Mg}$</td>
<td>-1.74087927E5+R<em>T</em>LN(9.96234977E-2)</td>
</tr>
<tr>
<td>MQ(HCP&amp;AG,AG,MG:VA)</td>
<td>$0_{Ag,Mg}^{Ag}$</td>
<td>-2.91748810E6+3.31001602E3*T</td>
</tr>
<tr>
<td>MQ(HCP&amp;AG,SN,MG:VA)</td>
<td>$0_{Sn,Mg}^{Sn,Ag}$</td>
<td>1.15310759E7-1.44608837E4*T</td>
</tr>
<tr>
<td>Sn diffusion</td>
<td>$Q_{Sn}^{Mg}$</td>
<td>-9.50964086E4+R<em>T</em>LN(1.47064452E-7)</td>
</tr>
<tr>
<td>MQ(HCP&amp;SN,SN,MG:VA)</td>
<td>$0_{Sn,Mg}^{Sn}$</td>
<td>-5.66233992E6+6.75973214E3*T</td>
</tr>
<tr>
<td>MQ(HCP&amp;SN,AG,MG:VA)</td>
<td>$0_{Sn}^{Ag,Mg}$</td>
<td>-5.10579233E6+6.34046674E3*T</td>
</tr>
</tbody>
</table>
Figure 4-1. Concentration-dependent interdiffusion coefficients of Mg/Mg-5Ag diffusion couples and the corresponding DICTRA simulations.
Figure 4-2. Temperature-dependent diffusion coefficients of Ag in Mg [40,67–70]. In the legend of Figure 4-2, Perp represents diffusion perpendicular to the c-axis, Para represents diffusion parallel to the c-axis, and PX represents diffusion in polycrystalline Mg.
Figure 4-3. Concentration profile of Mg/Mg-2Ag validation diffusion couple annealed at 525°C with corresponding DICTRA simulation.
Figure 4-4. Concentration-dependent interdiffusion coefficients of Mg/Mg-5Sn diffusion couples and the corresponding DICTRA simulations.
Figure 4-5. Temperature-dependent diffusion coefficients of Sn in Mg [40,68–71]. In the legend of Figure 4-5, Perp represents diffusion perpendicular to the c-axis, Para represents diffusion parallel to the c-axis, and PX represents diffusion in polycrystalline Mg.
Figure 4-6. Concentration profile of Mg/Mg-2Sn validation diffusion couple annealed at 525°C with corresponding DICTRA simulation.
Figure 4-7. Concentration-dependent interdiffusion coefficients of Mg/Mg-2Sn-5Ag diffusion couples and the corresponding DICTRA simulations.
Figure 4-8. Temperature-dependent diffusion coefficients of Ag in Mg and Ag in Mg-Sn.
Figure 4-9. Concentration profile of Mg/Mg-2Sn-5Ag validation diffusion couple annealed at 525°C with corresponding DICTRA simulation.
Figure 4-10. Concentration-dependent interdiffusion coefficients of Mg/Mg-2Ag-5Sn diffusion couples and the corresponding DICTRA simulations.
Figure 4-11. Temperature-dependent diffusion coefficients of Sn in Mg and Sn in Mg-Ag.
Figure 4-12. Concentration profile of Mg/Mg-2Ag-5Sn validation diffusion couple annealed at 525°C with corresponding DICTRA simulation.
CHAPTER 5
SUMMARY AND CONCLUSIONS

In an effort to increase fuel efficiency and decrease CO₂ emissions, the automotive industry is considering low-weight alternatives to current structural materials [11]. Magnesium alloys are being considered for such applications, as Mg is the lightest structural metal [11]. However, commonly used Mg alloys such as the AZ series have limited strength and creep resistance above 120°C, which limits their use in automotive applications [14]. The main cause of this poor performance at elevated temperatures is the discontinuous precipitation of the Mg₁₇Al₁₂ phase [19]. To address this, alloy development for Mg alloys without Al as an alloying element has begun [25,26]. Studies have identified the Mg-Sn system as a promising candidate for automotive applications, as the Mg₂Sn phase is stable at elevated temperatures [27,28]. However, the higher thermal stability achieved by Mg-Sn alloys comes with lower ductility and corrosion resistance [30]. Recent studies have shown that adding small amounts of Ag to Mg-Sn alloys can improve the ductility while still forming the desired Mg₂Sn precipitate, but much of the kinetics of the system is still not understood [31,32].

With the advent of improved computational methods and government efforts such as the Materials Genome Initiative, a focus has been placed on incorporating predictive computational models early on in the materials design process to reduce the number of experiments [33,34]. One example of such an approach is the CALPHAD methodology to materials design, which focuses on using the experimental descriptions of lower alloy systems in conjunction with thermodynamic and kinetic databases to predict the thermodynamics and kinetics of higher order systems where limited experimental data exists [35,36]. Following this CALPHAD approach, this study focused
on the development of kinetic experimental descriptions of the polycrystalline Mg-Ag, Mg-Sn, and the ternary Mg-Ag-Sn systems for use in Thermo-Calc’s kinetic database, DICTRA. Solid-solid diffusion couple experiments were performed and characterized with EPMA to quantify the concentration-dependent interdiffusion coefficient of Ag in Mg, Sn in Mg, Ag in Mg-Sn, and Sn in Mg-Ag. The interdiffusion coefficient data was extracted using the Sauer-Friese-den Broeder Method, and the data was optimized using the Parrot module of DICTRA. This yielded optimized atomic mobility parameters from each system, namely $Q^{Mg}_{Ag}$, $Q^{Mg}_{Sn}$, $Q^{Ag,Mg}_{Ag}$, $Q^{Sn,Mg}_{Sn}$, $Q^{Sn,Mg}_{Ag}$, and $Q^{Ag,Mg}_{Sn}$. A summary of all the solutes in the MGMOB1 database, along with the data from this study, can be found in Figure 5-1. It is important to note from Figure 5-1 that, as a result of this study, the kinetics of two additional ternary systems will be available for commercial use in Thermo-Calc’s Mg-based alloy kinetic database.

It was also shown that adding Sn to Mg-Ag and vice-versa has a significant effect on the activation energy of the diffusing species. In particular, adding Ag to Mg-Sn was found to increase the activation energy of Sn diffusion, which decreased the diffusion coefficient of Sn in Mg for temperatures below 500°C. Slower kinetics leads to greater coarsening resistance of precipitates, which allows the coarsening rate to be better controlled. Greater control of the coarsening rate, in turn, can lead to improved elevated temperature mechanical properties and creep resistance, making the Mg-Ag-Sn alloy system a promising candidate for use in weight-reducing automotive applications.
Figure 5-1. Temperature dependent diffusion coefficients of all relevant solutes in MGMOB1 with results of this study [40,67,68,72–74].
CHAPTER 6
FUTURE WORK

With the kinetics of the Mg-Ag-Sn system better understood, future work could include more diffusion couple experiments with the Mg-Ag-Sn system to further validate the atomic mobility parameters generated in this study. As the DICTRA database now contains only three ternary systems, future work could include kinetic assessments of other Mg-based ternary systems to add to the DICTRA database. Finally, with the kinetic assessment of the Mg-Ag-Sn system done in this study, the kinetics of quarternary systems containing Mg-Ag-Sn could be assessed. This would be done in conjunction with DICTRA, similar to this study.
Figure A-1. Mg-Ag phase diagram.
Figure A-2. Mg-Sn phase diagram.
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Figure A-4. Mg-Ag-Sn phase diagram at 500°C.
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Figure B-3. Concentration profile fit with cubic b-spline interpolation for Mg/Mg-5Ag diffusion couple annealed at 550°C.
Figure B-4. Concentration profile fit with cubic b-spline interpolation for Mg/Mg-5Sn diffusion couple annealed at 450°C.
Figure B-5. Concentration profile fit with cubic b-spline interpolation for Mg/Mg-5Sn diffusion couple annealed at 500°C.
Figure B-6. Concentration profile fit with cubic b-spline interpolation for Mg/Mg-5Sn diffusion couple annealed at 550°C.
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Figure D-9. Concentration profile of Mg-2Sn/Mg-2Sn-5Ag diffusion couple annealed at 550°C with corresponding DICTRA simulation.
Figure D-10. Concentration profile of Mg-2Ag/Mg-2Ag-5Sn diffusion couple annealed at 450°C with corresponding DICTRA simulation.
Figure D-11. Concentration profile of Mg-2Ag/Mg-2Ag-5Sn diffusion couple annealed at 500°C with corresponding DICTRA simulation.
Figure D-12. Concentration profile of Mg-2Ag/Mg-2Ag-5Sn diffusion couple annealed at 550°C with corresponding DICTRA simulation.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Joshua Wagner was born in 1993 in San Antonio, TX. In 2011, he graduated from the Collegiate High School at Northwest Florida State College in Niceville, FL. He obtained a Bachelor of Science degree in Materials Science and Engineering from the University of Florida in 2015. Joshua then accepted a Science and Engineering Palace Acquire position with the United States Air Force. He worked at Eglin Air Force Base from 2015 to 2016 before being sent back to the University of Florida to pursue a Master in Materials Science and Engineering degree at the University of Florida. His master’s work focused on the kinetic assessment of Mg-Sn, Mg-Ag, and Mg-Ag-Sn alloys for improved creep resistance. Joshua received his Master of Science in Materials Science and Engineering degree from the University of Florida in December 2017.