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INTERDIFFUSION AND IMPURITY DIFFUSION IN MAGNESIUM SOLID SOLUTIONS

by

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B.S. Missouri University of Science and Technology, 1994

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Materials Science and Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
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ABSTRACT

Magnesium, being lightweight, offers potential to be developed into extensive structural applications. The transportation segment has particular interest in Mg and Mg alloy for applications where reduced vehicle weight is proportional to increased fuel efficiency. Aluminum and zinc are two of the most common alloying elements in commercial Mg alloys. They improve the physical properties of Mg through solid solution strengthening and precipitation hardening. Diffusion plays a key role in the kinetics of and microstructural development during solidification and heat treatment. However, there is limited diffusion data available for Mg and Mg alloys. In particular, because Al is mono-isotopic, tracer diffusion data is not available. Interdiffusion of Mg solid solution with Zn also does not exist in literature.

The diffusional interaction of Al and Zn in Mg solid solution at temperatures ranging from 623 – 723K was examined using solid-to-solid diffusion couple method. The objective of this thesis is two-fold: first, is the examination of interdiffusion in the Mg solid solution phase of the binary Mg-Al and Mg-Zn systems; second, is to explore non-conventional analytical methods to determine impurity diffusion coefficients. The quality of diffusion bonding was examined by optical microscopy and scanning electron microscopy with X-ray energy dispersive spectroscopy, and concentration profiles were determined using electron probe microanalysis with pure standards and ZAF matrix correction. Analytical methods of concentration profiles based on Boltzmann-Matano analysis for binary alloys are presented along with compositional dependent interdiffusion coefficients. As the
concentration of Al or Zn approaches the dilute ends, an analytical approach based on the Hall method was employed to estimate the impurity diffusion coefficients.

Zinc was observed to diffuse faster than Al, and in fact, the impurity diffusion coefficient of Al was smaller than the self-diffusion coefficient of Mg. In the Mg solid solution with Al, interdiffusion coefficients increased by an order of magnitude with an increase in Al concentration. Activation energy and pre-exponential factor for the average effective interdiffusion coefficient in Mg solid solution with Al was determined to be 186.8 KJ/mole and $7.69 \times 10^{-1}$ m$^2$/sec. On the other hand, in the Mg solid solution with Zn, interdiffusion coefficients did not vary significantly as a function of Zn concentration. Activation energy and pre-exponential factor for the average effective interdiffusion coefficient in Mg solid solution with Zn was determined to be 129.5 KJ/mole and $2.67 \times 10^{-4}$ m$^2$/sec. Impurity diffusion coefficients of Al in Mg was determined to have activation energy and pre-exponential factor of 144.1 KJ/mole and $1.61 \times 10^{-4}$ m$^2$/sec. Impurity diffusion coefficients of Zn in Mg was determined to have activation energy and pre-exponential factor of 109.8 KJ/mole and $1.03 \times 10^{-5}$ m$^2$/sec. Temperature and composition dependence of interdiffusion coefficients and impurity diffusion coefficients are examined with respect to reported values in literature, thermodynamic factor, $\Phi$, diffusion mechanisms in hexagonal close packed structure, and experimental uncertainty.
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"The elementary diffusion process is so very fundamental and ubiquitous in the art and science of dealing with matter in its condensed phase that it never ceases to be useful but, at the same time, is a problem which is never really solved. It remains important by any measure."

D. Lazarus, 1984
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LIST OF ACRONYMS

$\nabla \mu$  Chemical potential gradient

$\eta$  Boltzmann variable

$\Phi$  Thermodynamic Factor

$\mu_i$  Chemical potential of component $i$

$v$  Kirkendall plane velocity

$A_I$  Interstitial solute atom

$\text{AI}$  Atom-Interstitial defect couple

$\text{Al}$  Aluminum

$A_S$  Substitutional solute atom

at.\%  Atomic percent

$\text{Au}$  Gold

$\text{AV}$  Atom-Vacancy defect couple

$\text{Be}$  Beryllium

$\text{BSE}$  Back-scattered electrons

$\text{Ce}$  Cerium

$C_i$  Concentration of component $i$

$C_i^\circ$  Concentration of component $i$ at Matano plane

$C_i^{\infty}$  Concentration of component $i$ at terminal end

$D$  Diffusion Coefficient (m$^2$/sec)

$D_o$  Pre-exponential factor (m$^2$/sec)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$\bar{D}$</td>
<td>Binary interdiffusion coefficient (m$^2$/sec)</td>
</tr>
<tr>
<td>$\bar{D}^{\text{eff}}$</td>
<td>Average effective interdiffusion coefficient (m$^2$/sec)</td>
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<tr>
<td>$D_I^I$</td>
<td>Intrinsic diffusion coefficient of component I (m$^2$/sec)</td>
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<tr>
<td>$D_I^*$</td>
<td>Impurity diffusion coefficient of component I (m$^2$/sec)</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
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<tr>
<td>EPMA</td>
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<td>erf</td>
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<tr>
<td>FCC</td>
<td>Face Centered Cubic crystal structure</td>
</tr>
<tr>
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</tr>
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<td>HCP</td>
<td>Hexagonal Close Packed crystal structure</td>
</tr>
<tr>
<td>I</td>
<td>Interstitial solvent atom</td>
</tr>
<tr>
<td>In</td>
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<tr>
<td>MA9</td>
<td>Mg-9wt.%Al</td>
</tr>
<tr>
<td>MAZ</td>
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</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>Mg(ss)</td>
<td>Magnesium solid solution</td>
</tr>
<tr>
<td>MZ6</td>
<td>Mg-6wt.%Zn</td>
</tr>
</tbody>
</table>
ORNL  Oak Ridge National Laboratory
Pb    Lead
Q     Activation energy (kJ/mole)
R     Ideal gas constant (8.314772 kJ/mole)
RPM   Revolutions per minute
RTD   Resistance Temperature Detector
§     Section
S     Vacancy Wind Factor
SE    Secondary Electrons
SEM   Scanning Electron Microscope
t    Time (seconds)
T     Temperature (Kelvin)
V     Vacancy
wt.%  Weight percent
Xi    Mole fraction of component i
x     Position (µm)
xo    Matano plane position
XEDS  X-ray Energy Dispersive Spectroscopy
ZAF   Atomic number, absorption, and fluorescence matrix correction factor
Z     Atomic number
Zn    Zinc
Z-score Standard score in normal distribution
While magnesium is abundant and lightweight, its poor cold forming properties and low ductility, limited high-temperature properties, and poor corrosion resistance have mandated alloy development. Two of the most common alloying elements in magnesium alloys are aluminum and zinc. Aluminum (FCC) and zinc (HCP) are relatively soluble in magnesium (HCP), but their solubility decreases at low temperatures. The substitutional solubility of aluminum in magnesium is $12.7 \text{ wt.}\%$ at $437 \degree C$ and $3.0 \text{ wt.}\%$ at $93 \degree C$; the substitutional solubility of zinc in magnesium is $6.2 \text{ wt.}\%$ at $340 \degree C$ and $2.8 \text{ wt.}\%$ at $204 \degree C$. Aluminum additions improve the strength and increase the solidification time. Magnesium alloys containing $6 \text{ wt.}\%$ aluminum have a good balance between strength and ductility while those that have more than $6 \text{ wt.}\%$ are age hardenable with the precipitation of $\text{Mg}_{17}\text{Al}_{12}$. Similarly, zinc is added, often times with aluminum, to magnesium in order to improve room temperature properties and corrosion resistance. Magnesium alloyed with zinc can be heat treated to form $\text{MgZn}$ precipitates. When added in amounts greater than $1 \text{ wt.}\%$ to magnesium alloys containing $7-10 \text{ wt.}\%$ aluminum, the alloy becomes more susceptible to hot shortness (ASM International, 1992). Diffusion is relevant to the rate of many microstructural changes that occur during processing of magnesium alloys.

Diffusion is the flux of atoms passing through an area in an increment of time. A number of atomic motion mechanisms have been proposed to explain the movement of solute atoms in a crystal lattice. In substitutional solid solutions, the diffusion atoms flow as a function of the solute concentration. The driving force for diffusion is the chemical
potential gradient or the decrease in molar free energy resulting from the dilution of solute atoms. In a diffusion couple, the chemical composition varies in the diffusion zone. Therefore, diffusing atoms continuously experience different chemical environments so the diffusion coefficient will vary through the zone. This situation, called interdiffusion, is usually concentration and temperature-dependent. While there are no known industry or agency standards established, a typical method for determining the interdiffusion coefficient, $\tilde{D}$, is to assemble two semi-infinite pure metals or alloys together and expose to a diffusion anneal.

Impurity diffusion is typically determined from temporal and spatial concentration data of an isotopic tracer solute. However, Al is mono-isotopic so enriched stable isotopes are not readily available and thus impurity diffusion data is limited. Darken related the concentration dependent diffusion coefficient to intrinsic diffusivity. Intrinsic diffusion is the rate of diffusivity of each element in the system relative to the lattice. Manning evolved Darken’s equation by incorporating the thermodynamic factor, $\Phi$, and vacancy-wind factor, $S$, to correlate the interdiffusion coefficient to tracer diffusion coefficients, $D^*_i$, in the binary system. In consideration of the Darken-Manning formalism, when the concentration of the solute goes to zero, both the thermodynamic and vacancy-wind factor go to unity. Thus, the interdiffusion coefficient can be equivocated to the impurity diffusion coefficient of an infinitely dilute solute in binary systems.

In an effort to improve fuel-efficiency and thereby reduce emissions, the Department of Energy has espoused efforts to extensively integrate the use of wrought magnesium into automotive applications. However, the limited design data and modeling
tools necessary for magnesium alloy development has consigned magnesium usage to die
cast applications. Therefore, fundamental diffusion data of technologically relevant
wrought magnesium alloy systems, Mg-Al and Mg-Zn, is presented herein.

In this study, the diffusion behavior in the solid solution regime in the binary Mg-Al
and Mg-Zn systems is explored through solid-to-solid diffusion couples. Interdiffusion
coefficients are calculated using the Boltzmann-Matano analysis and extrapolated to the
infinitely dilute compositions in an effort to determine impurity diffusion coefficients. An
analytical method of calculating impurity diffusion coefficients, first proposed by Hall,
which mitigates the error introduced by graphical integration, is also used to calculate
impurity diffusion coefficients. This method is validated by comparing outcomes obtained
in this study through solid-to-solid diffusion couples with results established through
conventional impurity diffusion studies using isotopic tracers. Finally, the relationship
between temperature and interdiffusion as well as impurity diffusion is examined thereby
revealing the nature of the pre-exponential factors and activation energies.
CHAPTER 2: LITERATURE REVIEW

Diffusion is the movement of atoms within a solution and can be described as a flux, $J$, of atoms passing through a unit area in a period of time thus $J_i = \frac{\text{mol}}{\text{meter}^2 \cdot \text{second}}$. In substitutional solid solutions, these atoms flow as a result of point defect motion which is related to the concentration of solute atoms, $C_i$, through Fick’s First Law (Fick, 1855) (Reed-Hill & Abbaschian, 1992). The net flux of diffusing matter passing normally through a unit area under the action of a concentration gradient, $\frac{dc_i}{dx}$, will move from high concentration to low concentration with a proportionality constant termed diffusion coefficient, $D_i$:

$$J_i = -D_i \frac{dc_i}{dx}$$

(1)

In general, it is more accurate to describe the diffusion flux as proportional to the chemical potential gradient, $\nabla \mu$. The gradient of chemical potential of the solute is the rate of change in energy resulting from the addition of the solute at constant temperature and pressure. As such, the gradient of chemical potential is the real driving force for diffusion and intermixing in a binary system (Mehrer, 2007).

2.1 Diffusion Mechanisms

Atoms move through solids by a number of different mechanisms. The diffusion mechanism employed depends on factors including crystal structure, solute size, and
intermolecular forces. Atomic motion can be broadly classified as independent movement or dependent movement. Independent movement involves the motion of an individual atom while dependent movement involves the motion of two or more atoms (Reed-Hill & Abbaschian, 1992). Several diffusion mechanisms have been proposed to explain atomic mobility in crystalline solids: Direct Exchange; Zener Ring; Interstitial; Interstitialcy; Vacancy; and Divacancy (Manning, 1968). With the exception of the direct exchange and Zener ring mechanisms, all diffusion mechanisms rely on the presence of point defects. Point defects include vacancies, self-interstitial atoms, substitutional impurity atoms and interstitial impurity atoms (Smallman & Ngan, 2007). Several types of point defects can coexist in real crystals; therefore several diffusion mechanisms can be simultaneously active.

For thermal diffusion of substitutional solid solutes in close packed structures, the direct exchange mechanism is energetically taxing and therefore not the favored mechanism for diffusion (Balluffi, Allen, & Carter, 2005). The Zener ring mechanism assumes thermal vibrations can provide enough energy to overcome the activation barrier for atomic migration. This mechanism also relies on the probability that a number of atoms, which form a ring in the lattice, will simultaneously jump to their associated nearest neighbor position. Zener showed through computation that a 4-atom ring has a sufficiently low potential energy barrier for conjoined motion compared to the activation energy of self-diffusion in a FCC crystal (Zener, 1950). However, extensive experimental results have manifested the Kirkendall effect which can only be rationalized through the vacancy mechanism (Reed-Hill & Abbaschian, 1992). Therefore, the ring mechanism, in the direct
exchange context, is not considered to be a probable mechanism for solid solution diffusion. The Kirkendall effect will be discussed further in terms of intrinsic diffusion coefficients.

Point defect mediated atomic migration mechanisms dominate current theory for substitutional solid solution diffusion. It is quite easy to conceive the interchange between a solute atom and a vacancy. At any given temperature, there is an equilibrium vacancy concentration. Unlike many other types of defects, vacancies will increase the entropy of the system therefore decrease the overall free energy. Therefore, the equilibrium vacancy concentration increases as temperature increases. However for diffusion to occur creating vacancies is not sufficient alone; vacancies must also be able to move or migrate. In order to have long range motion of the solute, the vacancy mechanism mandates the defect couples must continue to exchange positions with other sites thereby forming a continuous circuit (Bracht, 2000). Thus, the vacancy mechanism is much like the ring mechanism proposed by Zener except one atom is replace with a vacancy.

The exchange between a solute atom and a self-interstitial described by the interstitialcy mechanism is slightly different. The isolated point defect is coupled to the solute atom in order to minimize the local energy (Mehrer, 2007). The exchange propagates to the next nearest neighboring atom. However, because the energy of formation of self-interstitials is notably higher than the energy of formation for vacancies, interstitialcy is not commonly seen in thermal diffusion of metals (Murch, 2001).

Still another point defect mediated mechanism occurs in some metal systems when solute atoms dissolve at interstitial positions as well as substitutional sites. The solute
atoms can diffuse rapidly through the dissociative mechanism (Frank & Turnbull, 1956). In the dissociative mechanism the interstitial solute atom exchanges position with a substitutional vacancy and then dissociate to form a vacancy and an interstitial solute. The dissociative mechanism was first recognized in the Au-Pb system (Mehrer, 2007). This fast diffusion occurs in metals that have a large atomic radius relative to that of the substitutional solute but still have a large atomic radius ratio. For example, the atomic radius of the Pb solvent is 0.175nm and the Au solute is 0.144nm while radius ratio of the Au to Pb is 0.84. Solutes such as Au are called hybrid solutes (Bracht, 2000).

Fundamental diffusion mechanisms proposed for substitutional solid solutions are schematically presented in Figure 1. The solute atoms are denoted by a dark circular marker with an interior crosshatch. When vacancies are involved in the mechanism, they are indicated by open square markers. Atomic jump paths are represented by arrows. The upper left reaction signifies the interstitialcy mechanism given by the reaction $A_s + I \leftrightarrow AI$ where $A_s$ is the substitutional solute atom, $I$ is the interstitial solvent atom, and $AI$ is the defect couple. The vacancy mechanism is reflected in the upper right reaction and can be described as $A_s + V \leftrightarrow AV$ where $V$ is the vacancy and $AV$ is the defect couple. The lower left reaction represents the ring mechanism and the lower right reaction shows the disassociation mechanism which can be defined by $A_s \leftrightarrow A_i + V$ where $A_i$ is the interstitial solute.
Figure 1: Diffusion mechanisms in solid solutions: (Upper Left) Interstitialcy; (Upper Right) Vacancy; (Lower Left) Zener Ring; (Lower Right) Dissociative

There are two different types of atomic jumps that can occur in an HCP crystal. The first is a jump to the nearest neighbor within in the basal plane or along the a-axis while the second is a jump between the basal planes or along the c-axis. The probability of a successful jump can be viewed in terms of a frequency (Balluffi, Allen, & Carter, 2005). Therefore, Mg, with a c/a ratio of 1.62, will have varied jump distances parallel to the c-axis and the differing jump frequencies as a function of jump type. Self-diffusion and impurity diffusion is predicated by the simple migration barrier and frequency factors for vacancy
mediated diffusion (Allnatt & Lidiard, 1987). However, diffusion in concentrated solid solutions, interdiffusion, becomes more complex as short- and long-range order within the solution affect the correlation of jumps (Van der Ven & Ceder, 2005).

2.2 Diffusion Coefficients

2.2.1 Interdiffusion

In a binary diffusion couple, the chemical composition varies in the interdiffusion zone. Therefore, diffusing species continuously experience different chemical surroundings and, because the diffusion coefficient will depend on concentration, it too will vary through the zone (Mehrer, 2007). This scenario is designated as interdiffusion. Thus, Fick’s Second Law for diffusion in the x direction can be written as:

\[
\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left(\bar{D}_i \frac{\partial C_i}{\partial x}\right) = \bar{D}_i \frac{\partial^2 C_i}{\partial x^2} + \frac{d\bar{D}_i}{dC_i} \left(\frac{\partial C_i}{\partial x}\right)^2
\]  

(2)

where \(\bar{D}_i\) is the interdiffusion coefficient of component of \(i\). By assuming \(\bar{D}_i\) to be constant, Fick’s Second Law can be simplified to:

\[
\frac{\partial C_i}{\partial t} = \bar{D}_i \frac{\partial^2 C_i}{\partial x^2}
\]  

(3)

Composition-dependent diffusivity, \(\bar{D}\), can be determined from concentration profiles using Equation (3) when approached with the Boltzmann-Matano method or the
Sauer and Freise method (Mehrer, 2007). The former method is appropriate when there is no significant change in molar volume while the latter method is used when the molar volume of a diffusion couple changes substantially during interdiffusion (Heitjans & Karger, 2005).

2.2.1.1 Boltzmann-Matano Method

Boltzmann transformed the Fick’s Second Law, Equation (3), into a much simplified nonlinear ordinary differential equation from the nonlinear partial differential equation by utilizing a scaling parameter of distance, \( x \), over the square root of time (Boltzmann, 1894). Matano solved the ordinary differential equation by applying the initial and boundary conditions. The location of the Matano plane, or the plane of mass balance indicated as \( x_o \), is the position at which the condition is satisfied and is determined by integrating over the concentration profile (Matano, 1933).

\[
\int_{C_{i,\infty}}^{C_i^0} x dC_i + \int_{C_i^0}^{C_{i,\infty}} x dC_i = 0
\]  

(4)

where \( C_{i,\infty} \) and \( C_i^0 \) refer to the composition at terminal ends of the diffusion couple and \( C_i^0 \) is the composition at the Matano plane.
The interdiffusion flux of component, $\bar{J}_i$, is then calculated with respect to the position of the Matano plane. (Dayananda & Kim, 1979)

$$\bar{J}_i = \frac{1}{2t} \int_{c_i^+}^{c_i^0} (x - x_o) \, dC_i$$

(5)

The interdiffusion coefficient, $\bar{D}_i$, can then be calculated by combining Fick’s first law, given in Equation (1), with Equation (5) to yield,

$$\bar{D}_i = -\frac{1}{2t} \int_{c_i^+}^{c_i^0} \frac{\partial C_i}{\partial x} \, dC_i$$

(6)

2.2.2 Average Effective Interdiffusion

While the interdiffusion coefficient varies over the composition range, the average effective interdiffusion coefficient provides a single nominal coefficient for the compositional spectrum and allows for comparison with other diffusion coefficients as a function of temperature (Dayananda M., 1993). Additionally, in multicomponent systems, the effective interdiffusion coefficient alone provides information about the nature of the main and cross interdiffusion coefficients (Dayananda & Sohn, Average effective interdiffusion coefficients and their applications for isothermal multicomponent diffusion
couples, 1996). Integrating the flux over an interval from \( x_1 \) to \( x_2 \), and dividing by the change in composition over the interval, yields the effective interdiffusion coefficient, as:

\[
\bar{D}_{i}^{eff} = -\frac{\int_{x_1}^{x_2} j_{i} dx}{(c_{x_2} - c_{x_1})} \quad (i = 1,2, \ldots n)
\]  

\( 2.2.3 \) Intrinsic Diffusion

For many technologically relevant purposes, the interdiffusion coefficient, \( \bar{D}_{i} \) is a sufficient measure of the diffusion behavior of a binary substitutional system. Perhaps of greater fundamental interest however, are the rates of diffusion of individual components relative to local lattice planes. These rates are usually not equivalent. In an interdiffusion experiment, a net flux of atoms across any lattice plane exists; to conserve the density of lattice sites, the lattice plane shifts (Brandes & Brook, 1992). The intrinsic diffusion coefficient, \( D_{i}^{I} \) describes diffusion of the components relative to the lattice planes. This shift of lattice planes, known as the Kirkendall effect, is observed experimentally as a movement of inert markers (Reed-Hill & Abbaschian, 1992). Rapid surface oxidation typical of many magnesium alloys may serve as inherent markers thereby allowing for calculation of the Kirkendall velocity, \( v = \frac{x}{2t} \) where \( x \) is the distance the marker has shifted. Intrinsic diffusion, therefore, is proportional to the atomic jump frequency.
If the quantities of $\bar{D}_i$ and $\nu$ are known from experiment, the intrinsic diffusion coefficients can be deduced. For a binary system, $D^I_i$ can be related to $\bar{D}$ by Darken’s equation (Porter & Easterling, 1981) (Reed-Hill & Abbaschian, 1992):

$$
\bar{D} = X_AD_B^I + X_BD_A^I
$$

(8)

$$
\nu = (D_A^I - D_B^I) \frac{\partial X_A}{\partial x}
$$

(9)

where $X_A$ and $X_B$ are the atomic fraction of the components in the binary system.

### 2.2.4 Impurity Diffusion

Impurity diffusion is typically determined from temporal and spatial concentration data of an isotopic tracer solute. Manning evolved Darken’s equation by incorporating the thermodynamic factor, $\Phi$, and vacancy-wind factor, $S$, to correlate the interdiffusion coefficient to tracer diffusion coefficients, $D_i^*$, given as:

$$
\bar{D} = (X_AD_B^* + X_BD_A^*)\Phi S
$$

(10)

where $X_A$ and $X_B$ are the atomic fractions of components A and B in the binary system. (Manning, 1968) In consideration of the Darken-Manning formalism, when the
concentration of the solute goes to zero, both the thermodynamic and vacancy-wind factor go to unity. Thus, the interdiffusion coefficient can be equivocated to impurity diffusion coefficient of an infinitely dilute solute in binary systems.

2.2.4.1 Hall Method

At dilute compositional extremes, the Boltzmann-Matano graphical method may fail to provide adequate resolution to ascertain reliable interdiffusion coefficient and subsequent extrapolation of impurity diffusion coefficients. While the Boltzmann-Matano graphical analysis approach is a customary approach, there are a few reasons to consider an analytical solution for impurity coefficient applications. Specifically, since the position of the Matano plane is approximated by balancing the left and right side of the integral, and the area under the curve is determined by right-angled trapezoid summation over some interval of $x$, a degree of uncertainty can be introduced. Furthermore, the concentration gradient, $dC/dx$, is difficult to determine as the composition approaches that of the terminal ends. Using probability theory, L Hall proposed that, since time is constant for a given experiment, a probability plot of the concentration distribution will yield a straight line whose slope and intercepts can be used to solve the concentration dependent diffusion coefficient. (Hall, 1953) The Hall Method puts the concentration gradient in terms of a probability distribution permitting the determination of the interdiffusion coefficient at impurity levels. The basis of this method lies in acknowledging $C/C_\infty$ as a probability and thus writing it in terms of the standard normal cumulative distribution function or $C/C_\infty =$
\( \frac{1}{2} + \frac{1}{2} \text{erf } u \) where \( u = h\eta + k \) and \( \eta \) is the Boltzmann variable, \( x/2(t^{1/2}) \). As a result, the diffusion equation can be rewritten in terms of \( h, k, \) and \( u \) such that (Sarafianos, 1986):

\[
D = \frac{1}{h^2} + \frac{k\sqrt{\pi}}{h^2}(1 + \text{erf } u)\exp(u^2)
\]  

(11)

### 2.3 Temperature Dependence of Diffusion

Solid-state diffusion is strongly dependent on temperature. In general, diffusion increases with increasing temperature. The temperature dependence of diffusion coefficients typically fits an Arrhenius model. For example, Equation (12) shows the relation between the interdiffusion coefficient and temperature.

\[
\bar{D} = \bar{D}_0 e^{-\frac{\bar{Q}_D}{RT}}
\]  

(12)

\( \bar{D}_0 \) is the pre-exponential factor and \( \bar{Q}_D \) is the activation energy for interdiffusion. Temperature is the absolute temperature and \( R \) is the gas constant. When the diffusion coefficient is plotted against the inverse of the temperature, the slope of the line will give the activation energy and the intercept will yield the pre-exponential as shown in Figure 2.
Figure 2: Schematic representation of the Arrhenius relationship between diffusivity and temperature

The physical meaning of the pre-exponential factor and activation energy depends on the diffusion mechanism, on the type of diffusion process, and on the lattice geometry (Mehrer, 2007). In substitutional solid solutions, the attractive and repulsive forces between solute atoms and vacancies affect the probability of a vacancy existing on a nearest-neighbor position of a solute atom (Mehrer, 2007). Additionally, there exists a correlation between the directions of consecutive jumps; the probability of making a jump depends on the direction of the preceding jump (Balluffi, Allen, & Carter, 2005). The
predominant diffusion mechanism will govern the correlation and frequency. The diffusion coefficient can provide some insight into correlation factor, jump attempt frequency, and binding energy, when the vacancy mechanism is assumed.

2.4 Diffusion in the Mg-Al Binary System

Diffusion in the Mg-Al system was investigated by Brennan through solid diffusion couples of pure Mg and Al in the temperature range of 523-673K (Brennan, Bermudez, Kulkarni, & Sohn, Interdiffusion in the Mg-Al system and intrinsic diffusion in Mg2Al3, 2012). The formation and growth of the intermetallic phases, β-Mg2Al3 and γ-Mg17Al12, and the absence of the ε-Mg23Al30 phase was observed at all examined temperatures, as shown in Figure 3. The β-Mg2Al3 phase grew thicker and had higher parabolic growth constants with lower activation energy for growth. Concentration-dependent interdiffusion coefficients were determined from the concentration profile using the Boltzmann-Matano Method with appropriate correction for changes in molar volume of intermetallic phases. Interdiffusion in the β-Mg2Al3 phase was the fastest, followed by the γ-Mg17Al12 phase, the Al solid-solution and the Mg solid-solution, in decreasing order respectively. Intrinsic diffusion coefficients at the marker plane composition of 38 at.% Mg in the β-Mg2Al3 were determined. The Al intrinsic diffusion was higher than the Mg intrinsic diffusion.
Figure 3: Backscatter electron micrographs from Mg vs. Al diffusion couples annealed at (a) 573K for 720 hours, (b) 623K for 360 hours, and (c) 673K for 240 hours. \( x_m \) is the marker plane. (Brennan, Bermudez, Kulkarni, & Sohn, Interdiffusion in the Mg-Al system and intrinsic diffusion in Mg2Al3, 2012)

The impurity diffusion of Al in single crystal Mg was investigated with first-principles density functional theory in the local density approximation (Ganeshan, Hector Jr., & Liu, 2011). Impurity diffusion within the basal plane was found to be slightly higher than Al impurity diffusion between the basal planes. The activation energy and pre-exponential factor was reported to be 137.0 kJ/mole and 4.24x10^{-6} m^2/s, respectively in the basal plane (\( \perp \)), and 142.8 kJ/mole and 7.14x10^{-6} m^2/s, respectively in the normal plane. Impurity diffusion was also studied by Brennan through depth profiling of thin Al film on Mg substrate in the temperature range of 523-673K (Brennan, et al., Aluminum Impurity Diffusion in Magnesium, 2012). In this study, the activation energy and pre-exponential factor of Al in Mg was determined as 155 kJ/mole and 3.9x10^{-3} m^2/s, respectively. However, the diffusion coefficients were reported to be elevated in comparison to the modeled coefficients as a result of experimental approach.
2.5 Diffusion in the Mg-Zn Binary System

Brennan also studied diffusion in the Mg-Zn system through solid diffusion couples of pure Mg and Zn in the temperature range of 568-598K (Brennan, Bermudez, Kulkarni, & Sohn, Diffusion Couple Investigation of the Mg-Zn System, 2012). The formation and growth of the intermetallic phases MgZn$_2$, Mg$_2$Zn$_3$, and Mg$_2$Zn$_{11}$ phases were identified in all three couples and the Mg$_{51}$Zn$_{20}$ phase in the 598K couple, as shown in Figure 4.

Calculation of the parabolic growth constants presented MgZn$_2$ as having the highest growth rate followed by the Mg$_2$Zn$_3$ phase and the Mg$_2$Zn$_{11}$ phase. The activation energy for growth was calculated to be 105 kJ/mole for the Mg$_2$Zn$_3$ phase and 207 kJ/mole for the MgZn$_2$ phase. Integrated interdiffusion coefficients were determined for each phase formed. Interdiffusion in the MgZn$_2$ phase was the fastest, followed by the Mg$_4$Zn$_7$ phase and then Mg$_2$Zn$_{11}$.

![Figure 4: Representative backscatter electron images of Mg vs. Zn diffusion microstructures at (a) 568 for 384 h, (b) 588K for 168 h, and (c) 598K for 120 h. Xm is the marker plane. [Note: Mg$_2$Zn$_{11}$ in (a) is largely pulled out from the diffusion couple.] (Brennan, Bermudez, Kulkarni, & Sohn, Diffusion Couple Investigation of the Mg-Zn System, 2012)](image-url)
Ganeshan, et al., analyzed Zn impurity diffusion in single crystal Mg using the 8-frequency model for impurity diffusion in HCP metals (Ganeshan, Hector Jr., & Liu, 2011). In contrast to the kinetic behavior of Al impurities in Mg, substantial differences in activation energy and pre-exponential factor for Zn impurity diffusion in Mg were reported for diffusion parallel to the c-axis and within the basal planes. The activation energy and pre-exponential factor was reported to be 126.9.3 kJ/mole and 7.3x10^-7 m^2/s, respectively in the basal plane, and 126.0 kJ/mole and 7.82x10^-6 m^2/s, respectively normal to the basal plane (Ganeshan, Hector Jr., & Liu, 2011). Zn impurity diffusion is significantly faster along the c-axis than along the basal plane. The modeling does not purport to be representative of the kinetic behavior in polycrystalline Mg. Lal studied Zn impurity diffusion in polycrystalline Mg using the 65Zn isotope in the temperature range of 740 to 893K (Lal, 1967). The tracer diffusion experimental approach yielded impurity diffusion coefficients substantially higher than that determined with the single-crystal modeling approach. Lal reported an activation energy and pre-exponential factor of 119.9 kJ/mole and 3.85x10^-5 m^2/s, respectively (Lal, 1967). Similarly, Čermák used conventional isotopic tracer techniques to determine the Zn impurity diffusivity in Mg in the temperature range of 648 to 848K (Čermák & Stoukal, 2006). The activation energy and pre-exponential factor was found to be 128.9 kJ/mole and 1.73x10^-4 m^2/s, respectively. There is good agreement between the impurity diffusion coefficient profiles as a function of temperature reported by Lal and Čermák. Combining their experimental results, the activation energy and pre-exponential factor is 125.2 kJ/mole and 1.0x10^-4 m^2/s, respectively (Neumann & Tuijn, 2009). Brennan determined Zn impurity diffusion coefficients through extrapolation of
interdiffusion coefficients ascertained from a solid-to-solid couple annealed at 598K. The impurity diffusion of Zn in Mg at 598K was reported as $D=8.5 \times 10^{-17}$ m$^2$/s (Brennan, Bermudez, Kulkarni, & Sohn, Diffusion Couple Investigation of the Mg-Zn System, 2012). This diverged from published experimental data but was in good agreement with modeled single crystal data, as shown in Figure 5.

Figure 5: Zn Impurity diffusion in Mg as a function of inverse temperature. Fitted line using $D_0=1.0 \times 10^{-4}$ m$^2$/s and $Q=125.7$ kJ/mole. (Lal, 1967) (Čermák & Stoukal, 2006) (Ganeshan, Hector Jr., & Liu, 2011) (Neumann & Tuijn, 2009)
CHAPTER 3: EXPERIMENTAL DETAILS

3.1 Materials

The diffusion behavior in the Mg-Al-Zn ternary system was investigated through solid-to-solid diffusion couples. Binary solid solution Mg alloys, Mg-9wt.%Al (MA9) and Mg-6wt.%Zn (MZ6), were coupled to pure Mg to gain insight into the concentration dependent interdiffusion and impurity diffusion of Al and Zn in Mg. Table 1 presents the examined couples. The pure Mg (Polycrystalline, 99.9%) was commercially procured from Alfa Aesar while the magnesium alloys were produced by Magnesium Elektron, North America. The chemical analysis for the alloys and pure Mg is identified in Table 2.

<table>
<thead>
<tr>
<th>Material A</th>
<th>Material B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>MA9</td>
</tr>
<tr>
<td>Mg</td>
<td>MZ6</td>
</tr>
</tbody>
</table>

Table 2: Chemical analysis for pure Mg and Mg alloys

<table>
<thead>
<tr>
<th></th>
<th>Mg wt.% (at.%)</th>
<th>Al wt.% (at.%)</th>
<th>Zn wt.% (at.%)</th>
<th>Others wt.%</th>
<th>Each wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>99.95 (100.00)</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.00)</td>
<td>&lt;0.05</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>MA9</td>
<td>90.38 (91.27)</td>
<td>9.59 (8.72)</td>
<td>0.016 (0.01)</td>
<td>&lt;0.02</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>MZ6</td>
<td>93.74 (97.58)</td>
<td>0.01 (0.01)</td>
<td>6.23 (2.41)</td>
<td>&lt;0.02</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

The alloys were direct chill cast into roughly 1.5" diameter billets 4" in length. The billets were scalped, removing the outer contaminated skin, and preheated in an inert
atmosphere at 673K for one hour prior to extrusion. The extruded rod had a final diameter of 9mm. All material was subjected to a grain-growth anneal roughly 40 – 50K below solidus for 8 – 16 hours. The grain size was reported to be between 100 – 500μm. The material was then sectioned into 3 – 4 mm thick discs. The serialized disks were provided by Oak Ridge National Lab (ORNL), Oak Ridge, TN, USA.

3.2 Diffusion Couple Assembly

The serialized discs were prepared for diffusion bonding by incrementally polishing the surface down to 1 μm using ethyl alcohol as a non-oxidizing lubricant. An intimate interface between two or more disks was achieved with the aid of a clamping jig. Constant and uniform clamping force could be achieved with standard 317L steel jigs rather than those made with low thermal expansion Kovar. The assembly jig, shown in Figure 6, consisted of two steel plates pulled together with three screws. Since formal standards had not been developed for diffusion couple assembly, tribal protocols for incrementally tightening the jig to an approximate uniform clamping force, determined through visual and tactile evaluations, were utilized. Alumina spacers were used between the steel plates and sample disks and served to inhibit diffusion bonding between the steel and the disk.

The loaded jig was placed in a quartz ampoule with a small strip of tantalum foil. Tantalum was intended to absorb oxygen evolved at elevated temperatures. The ampoule was open on one end and had a tapered stem on the other. A quartz cap was welded onto the open end of the ampoule using standard flameworking techniques. The stem of the ampoule was attached to a custom built vacuum system capable of pulling down to ~10⁻⁹
atm (10⁻⁶ Torr) as well as injecting hydrogen or argon gas. The ampoule was flushed with hydrogen and argon and then fully evacuated before the stem was removed from the capsule. An encapsulated diffusion couple assembly is shown in Figure 7.

Figure 6: Schematic of solid-to-solid diffusion couple jig

Figure 7: Encapsulated diffusion couple assembly
3.3 Diffusion Anneal

The encapsulated assemblies were instrumented with resistance temperature detectors (RTD) calibrated and supplied by ORNL. The RTDs very accurately correlate the resistance across the sheathed element with temperature. The instrumented capsule was placed in either a Paragon Bluebird™ furnace or a Lindberg™ three-zone tube furnace preheated to the annealing temperature. The temperature of the diffusion couples was monitored via the independent RTD probe through an Omega data acquisition system which also recorded the thermal profiles of ramp-up and quench-down to verify furnace temperature stability.

Each diffusion couple system was annealed at three different temperatures. Diffusion anneal temperatures were selected by considering the phase diagram as well as previous diffusion study temperatures. The diffusion anneal time was established by targeting a zone thickness, $x$, of 100 μm. Thus, diffusion times were deduced by analysis and in conjunction with the characteristic diffusion zone thickness expressed as

$$x_i = \sqrt{t \cdot D_0 \exp \left( \frac{Q_i}{RT} \right)}$$

(Dayananda & Sohn, Average effective interdiffusion coefficients and their applications for isothermal multicomponent diffusion couples, 1996). Diffusion anneal temperatures and times are detailed in Table 3.
Table 3: Diffusion anneal temperature and time parameters

<table>
<thead>
<tr>
<th>Couple</th>
<th>Temperature (°C)</th>
<th>Time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg vs. MA9</td>
<td>623</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>24</td>
</tr>
<tr>
<td>Mg vs. MZ6</td>
<td>623</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>24</td>
</tr>
</tbody>
</table>

After the annealing cycle, the capsules were quickly removed from the furnace and quenched in water at room temperature to halt the diffusion process. The couple was extracted from the jig and cold mounted in epoxy. Once cured, the couple was cross-sectioned and metallographically prepared down to 1μm finish, again using non-oxidizing lubricants.

Particular care had to be taken during metallographic sample preparation to preclude debonding in the interdiffusion zone. Grinding was accomplished with 600grit SiC abrasive paper and is followed by pentastep diamond polishing sequence starting at 30μm and incrementally reducing to 1μm. All grinding and polishing was contra-rotational and typically with 5 – 10N force. Grinding took place at 300 RPM while polishing was limited to 150 RPM. No water was used and acetone exposure was minimized to mitigate oxidation of the reactive Mg surface. Grinding was accomplished using Ethyl Alcohol and polishing was done with a lubricating mineral oil. A final manual polish was accomplished with 1μm Al₂O₃ in denatured ethanol. An ultrasonic bath was utilized between steps to ensure complete removal of grinding and polishing debris.
3.4 Interdiffusion Zone Characterization

Each diffusion couple was first examined using optical microscopy to check the diffusion bond integrity. Figure 8 is a photograph of a metallographically prepared diffusion couple. The faying surface is evident from the step along the couple edge and an interface, vaguely discernible in this figure, can be revealed with low magnification (<100X).

![Figure 8: Photograph of cross-sectioned diffusion couple.](image)

A Scanning Electron Microscope equipped with an X-ray Energy Dispersive Spectrometer (Zeiss Ultra 55 SEM with XEDS) was used to confirm diffusion and to determine the thickness of the interdiffusion zone (IZ). In scanning electron microscopy, an electron beam is rastered across the specimen. The primary electrons interact with the
specimen generating secondary electrons (SE), backscattered electrons (BSE), and characteristic x-rays. Secondary electrons give topographical information about the specimen and, on polished solid solution samples, are not overtly informative in the characterization of the interdiffusion zone of solid solutions. Backscattered electrons, on the other hand, are attenuated by variations in the atomic number of the constituents with heavier elements backscattering more electrons and thus imaging brighter. Therefore, compositional differences can be visually observed when there are sufficient differences in the atomic number of the elements. Since the atomic number of Mg (Z=12) and Al (Z=13) differ by only one, no contrast can be discerned; contrast differentiation of Mg and/or Al from Zn (Z=30) was somewhat more evident. Therefore, electron micrographs of the Mg vs. MA9 and Mg vs. MZ6 diffusion couples were visually nondescript. The most meaningful information from SEM came from the generation of characteristic x-rays which could be used to ascertain chemical information and map the compositional changes across the scanned region. Using XEDS, qualitative compositional profiles were generated which allowed for the determination of interdiffusion zone thickness. The extent of the IZ was dependent on the composition of the couple and diffusion anneal parameters. The IZ for each couple was a rough approximation based on empirical data collected during SEM and XEDS evaluations rather than a calculated distance.

Electron Microprobe Analysis (JEOL JXA-8200 EMPA) was used for quantitative chemical analysis of the diffusion zone on a micron-scale. Electron microprobe analysis (EPMA) allowed for accurate compositional characterization across the diffusion zone. The nondestructive technique employs characteristic x-rays excited by a finely focused electron
beam incident on a flat surface of the sample to determine the concentration profile. The JEOL JXA-8200 electron microprobe is equipped with wavelength-dispersive spectrometers to provide a complete quantitative chemical analysis via x-ray emission spectral analysis. Analyses were acquired using Probe For EPMA software and measured x-ray intensities were corrected for matrix affects by applying the Heinrich ZAF correction factors. MAZ Alloy standards were used for equipment calibration. Typical operating conditions were 7.5 keV accelerating voltage for Mg vs. MA9 and 15 keV for Mg vs. MZ6; probe current was 50 nA.

Multiple line scans were performed on the central region of each bonded couple thereby mitigating the potential for anomalous results induced by edge effects. A minimum of 30μm separated the line scans. The scans were performed orthogonal to the interface extending approximately 50μm beyond IZ as indicated schematically in Figure 9. All EMPA scans were performed at ORNL.
3.5 Quantitative Analysis

Fitted concentration profiles were extracted from the EPMA data using either a cubic smoothing spline or a Savitzky-Golay smoothing function in OriginPro 8.6 software (Savitzky & Golay, 1964). The smoothing splines is a global cubic B-spline interpolation with a smoothing factor and is continuous up to a 2nd order derivative but winds around the original data points rather than passing through them. Savitzky-Golay smoothing is a local least-squares polynomial regression within each window of a specified number of data points, creating a new, smoothed value for each data point, but may not have a continuous derivative. Both methods preserve the overall profile of the data which is often lost when smoothing by adjacent averaging. Each piecewise spline used to fit the
concentration profiles in this study represented 4 to 10 evenly spaced EPMA data points. As a result, each concentration profile consists of 10 to 40 piecewise cubic splines. The schematic presented in Figure 10 presents a typical concentration profile. The EPMA data is represented by open circles; the cubic spline and Savitzky-Golay fits are offset for clarity.

Figure 10: Representation of typical measured solute concentration data and offset fitted concentration profiles
Analytical methods for analysis of concentration profiles based on the classical Boltzmann-Matano method for binary alloys as described in §2.2.1.1 were utilized. Because the couple compositions are restricted to the solid solution regime, molar volume effects can be ignored. Fundamental to the Boltzmann-Matano method is the ability to precisely determine the position of the Matano plane. Numerical integration of the definite integral given in the equation of mass balance, Equation (4), allows the position of the Matano plane to be determined. Since the fitted concentration profile is a set of discrete values rather than a function, pairs of adjacent values were used to form right angled trapezoids for approximation of the integral. However, the error introduced through this method led to a loss of precision in the position of the Matano plane. Based on diffusion theory, the flux at the terminal ends will be zero while it will be the extremum at the Matano plane. Using the flux equation given in Equation (5), the position of the Matano plane was iteratively adjusted until the flux profile went to zero at the terminal ends.

Composition-dependent interdiffusion coefficients in MgAl- and MgZn-solid solutions were calculated as were average effective interdiffusion coefficients. The average effective interdiffusion coefficients were plotted as a function of temperature and the pre-exponential coefficient and activation energy was calculated for the binary systems. Using the Hall Method, binary impurity diffusion coefficients were calculated and compared to those determined through extrapolation of the Boltzmann-Matano interdiffusion coefficient as well as to literature values. It was expected, as previously mentioned, that the surface oxide inherent to the specimens at assembly would provide a discernible marker beneficial for subsequent analysis. However, measurable and significant differences
between the marker plane and Matano plane could not be determined. As a result, the Kirkendall shift was not calculated for any couple and intrinsic diffusivity has not been established.
CHAPTER 4: RESULTS AND ANALYSIS

4.1 Diffusion Couples Mg vs. MA9

The diffusion anneal parameters for the Mg vs. MA9 couples were presented in Table 3. The fitted concentration profiles are shown with the raw EPMA data in Appendix A. The asymptotic regions do not mirror each other indicating a concentration dependence on the diffusivity but also presenting additional challenges for reliable curve fitting. Some fitted concentration profiles discrepancies, such as an abrupt change in the slope, can adversely impact the calculated diffusion coefficient. Therefore, not all fitted line scans were used for all calculations. In addition, some EPMA data was so erroneous they were excluded from the fitting process. The most common source of scatter in the EPMA data was surface asperities of the cross-sectioned diffusion couple. Line scan #1 (LS1) for the couple annealed at 673K was not fit nor used in calculations because the data was significantly distorted in terms of peak concentration and concentration gradient. In this case, the line scan orientation was not orthogonal to the interface.

The concentration dependent interdiffusion coefficients were calculated for the Mg vs. MA9 couples using the Boltzmann-Matano method. The Matano plane position and concentration was determined for each fitted concentration profile. Diffusion theory dictates the concentration at the Matano plane should be consistent between individual line scans of the same couple. Experimental and analytical factors can introduce error. Therefore, to ensure integrity of the diffusion data generated, line scans which yielded anomalous Matano compositions were excluded from Boltzmann-Matano analysis. Table 4
presents the Matano composition for all fitted Mg vs. MA9 line scans. At 623K, LS3 could not be reliably fit through the entire composition range. The poor fit resulted in an abrupt change in slope and is evident as a kink in the concentration profile. Nonetheless, the fitted data for this line scan did not diverge substantially and could be used to evaluate the Matano composition. As can be seen, the LS2 of the couple annealed at 623K and LS1 of the 723K couple are out of family in terms of composition at the Matano plane.

Table 4: Composition at the Matano plane for the Mg vs. MA9 couples

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Line Scan</th>
<th>Composition (at.% Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>623</td>
<td>LS1</td>
<td>4.651</td>
</tr>
<tr>
<td></td>
<td>LS2</td>
<td>5.785</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>4.410</td>
</tr>
<tr>
<td>673</td>
<td>LS2</td>
<td>5.363</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>5.398</td>
</tr>
<tr>
<td>723</td>
<td>LS1</td>
<td>5.068</td>
</tr>
<tr>
<td></td>
<td>LS2</td>
<td>5.552</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>5.564</td>
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</tbody>
</table>

The calculated interdiffusion coefficients as a function of Al concentration is presented in Figure 11. The composition dependent diffusion coefficients for the couple annealed at 623K are consequent of only LS1 since the other line scans could not be adequately fit. The open markers shown for the 723K and 673K indicate the coefficients calculated based on the LS2 scans while the solid marker corresponds to data derived from the LS3 scan. The profile trends upward from the left to the right; this positive trend is more evident as the temperature increases. Since the addition of Al decreases the melting point of the MgAl solid solution, interdiffusion coefficients would be expected to increase.
with increasing Al content if predicated on the equilibrium vacancy concentration alone. While this presumption is valid for self-diffusion and impurity diffusion, it is not valid for interdiffusion. The implications of the trend will be discussed further in §5.1. At the lowest temperature, the interdiffusion appears to be independent of concentration, remaining virtually constant throughout the examined compositional range. There is an obvious offset in the interdiffusion profile at 6.5 at.% Al. This offset in the diffusion profile may indicate a change in diffusion mechanism or could be an artifact of the curve fitting protocol.

Figure 11: Mg vs. MA9 Boltzmann-Matano interdiffusion coefficient as a function of Al concentration
The average effective interdiffusion coefficient for the Mg-Al solid solution phase was established for the entire concentration range using Equation (7). From the Arrhenius relationship, the activation energy and pre-exponential factor was calculated. Table 5 presents the results of the effective interdiffusion analysis valid for MgAl solid solution containing up to 8.5 at.\% Al.

Table 5: Average effective interdiffusion coefficients, pre-exponential factor, and activation energy for interdiffusion in MgAl solid solution

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$D_{\text{eff}}$ m$^2$/sec</th>
<th>Individual</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>623K</td>
<td>1.38x10^{-16}</td>
<td>1.38x10^{-16}</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>673K</td>
<td>3.09x10^{-15} 4.12x10^{-15}</td>
<td>3.61x10^{-15} 7.25x10^{-16}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>723K</td>
<td>1.95x10^{-14} 1.99x10^{-14}</td>
<td>1.97x10^{-14} 2.88x10^{-16}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_0$ (m$^2$/sec)</td>
<td>0.769</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q$ (kJ/mole)</td>
<td>186.8</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Graphical extrapolation of $\bar{D}$ to the $X_{\text{Al}} = 0$ can be directly equivocated to impurity diffusion coefficients, $D^*$, as described by the Darken-Manning formalism given in Equation (10). The extrapolated pre-exponential factor and activation energy for Al impurity diffusion in Mg is 6.2x10^{-4} m$^2$/sec and 152.7 kJ/mole, respectively. The results of the graphical extrapolation are presented in Table 6.
Table 6: Boltzmann-Matano Al extrapolated impurity diffusion coefficients, pre-exponential factor, and activation energy

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$D_{Al}^+$ (m$^2$/sec)</th>
<th>Individual</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>623K</td>
<td>1.05x10^{-16}</td>
<td>1.05x10^{-16}</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>673K</td>
<td>7.6x10^{-16}</td>
<td>7.17x10^{-16}</td>
<td>6.15x10^{-17}</td>
<td></td>
</tr>
<tr>
<td>723K</td>
<td>6.62x10^{-15}</td>
<td>6.29x10^{-15}</td>
<td>4.74x10^{-16}</td>
<td></td>
</tr>
<tr>
<td>$D_0$ (m$^2$/sec)</td>
<td>6.2x10^{-4}</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q$ (kJ/mole)</td>
<td>152.7</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, when the composition approaches infinite dilution, the graphical method of determining interdiffusion coefficients can become fraught with error. Thus, the analytical approach purported by Hall was used to determine the interdiffusion coefficient for Mg$_{Al}$ solid solution compositions less than 1 at. % Al. A fundamental presumption of the Hall method is the concentration in the interdiffusion zone, at constant temperature, is analytically modeled by the Gaussian probability density function and the gradient at the low concentration region can be described by the standard normal cumulative distribution function. Since the Hall Method only considers the low concentration region, the interdiffusion coefficient was calculated for all fitted line scans as all had seemingly good fits. Figure 12 shows the representative continuity in interdiffusion coefficients calculated using the graphical Boltzmann-Matano method at compositions >1 at. % Al, and the analytical Hall method at compositions < 1 at. % Al. For graphical clarity, only one line scan for each couple is presented.
Using the Hall diffusion coefficient at the compositional minima, the activation energy and pre-exponential factor of the impurity diffusion was ascertained. The pre-exponential factor and activation energy for Al impurity diffusion in Mg is $1.20 \times 10^{-4} \text{ m}^2/\text{sec}$ and $142.5 \text{ kJ/mol}$, respectively. However, the compositional minima is not at zero and so, to better capture the Al impurity diffusion coefficient of the infinitely dilute Mg$_{Al}$ solid solution, the Hall interdiffusion profiles were extrapolated to zero concentration. The resulting activation energy and pre-exponential factor for Al impurity diffusion in Mg is $1.61 \times 10^{-4} \text{ m}^2/\text{sec}$ and $144.1 \text{ kJ/mol}$, respectively. Table 7 presents a comparison between the extrapolated results and the concentration minima results. Regardless of the approach in extracting the impurity diffusion coefficient using the Hall Method, the results yield slightly different results than the graphical extrapolation of the Boltzmann-Matano method. The activation energy for Al impurity diffusion is markedly lower than the average effective interdiffusion activation energy, which was $186.8 \text{ kJ/mol}$. 
Figure 12: Interdiffusion coefficients as a function of Al composition calculated using the graphical Boltzmann-Matano method at compositions >1 at.% Al and the analytical Hall method at composition < 1at.% Al.
### Table 7: Hall Al impurity diffusion coefficients pre-exponential factors, and activation energies

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Composition Minima</th>
<th>Extrapolation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_A (m^2/sec)$</td>
<td>$D_A (m^2/sec)$</td>
</tr>
<tr>
<td></td>
<td>Individual Average Std. Dev.</td>
<td>Individual Average Std. Dev.</td>
</tr>
<tr>
<td>623</td>
<td>$8.30 \times 10^{-17}$ $1.34 \times 10^{-16}$ $4.40 \times 10^{-17}$</td>
<td>$8.39 \times 10^{-17}$ $1.59 \times 10^{-16}$ $4.12 \times 10^{-17}$</td>
</tr>
<tr>
<td>673</td>
<td>$1.28 \times 10^{-15}$ $1.07 \times 10^{-15}$ $2.94 \times 10^{-16}$</td>
<td>$1.29 \times 10^{-15}$ $9.00 \times 10^{-16}$ $2.76 \times 10^{-16}$</td>
</tr>
<tr>
<td>723</td>
<td>$5.20 \times 10^{-15}$ $6.01 \times 10^{-15}$ $8.10 \times 10^{-16}$</td>
<td>$5.74 \times 10^{-15}$ $6.11 \times 10^{-15}$ $6.14 \times 10^{-15}$ $8.10 \times 10^{-16}$</td>
</tr>
<tr>
<td>$D_o (m^2/sec)$</td>
<td>$1.20 \times 10^{-4}$ --</td>
<td>$D_o (m^2/sec)$ $1.61 \times 10^{-4}$ --</td>
</tr>
<tr>
<td>$Q (kJ/mole)$</td>
<td>142.5 --</td>
<td>$Q (kJ/mole)$ 144.1 --</td>
</tr>
</tbody>
</table>

#### 4.2 Diffusion Couples Mg vs. MZ6

The diffusion anneal parameters for the Mg vs. MZ6 couples were identified in Table 3. The fitted concentration profiles are shown with the raw EPMA data in Appendix B. The minimal divergence of symmetry in the concentration profile, in particular those from diffusion couples annealed at 673K and 723K, implies interdiffusion in the Mg-Zn solid solution is not strongly concentration dependent. However, at the lowest anneal temperature, 623K, asymmetry of the concentration profile and the sharp change in the concentration gradient imply a notable change in the diffusion coefficient. As was the case in the Mg vs. MA9 system, not all EPMA data was used to fit the concentration profiles and
not all fitted line scans were used for all calculations. However, all line scans were fit. Close examination of the fitted concentration profiles for LS1 and LS3 of the couple annealed at 623K reveals an uncharacteristic fluctuation.

To determine the validity of an individual fit concentration profile, the Matano plane position and concentration was determined. While LS1 and LS3 of the 623K couple have erroneous kinks in the fitted profile, the digression from fit does not adversely affect the determination of the Matano plane and corresponding composition. As was done in the Mg vs. MA9 couple, these profiles were included for Matano composition comparisons. Line scans which yielded inconsistent Matano compositions were excluded from Boltzmann-Matano analysis. Table 8 presents the Matano composition for all fitted Mg vs. MZ6 line scans. As can be seen, LS3 of the couples annealed at 623K and at 673K couples are disparate.

Table 8: Composition at the Matano plane for the Mg vs. MZ6 couples

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Line Scan</th>
<th>Composition (at.% Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>623</td>
<td>LS1</td>
<td>0.804</td>
</tr>
<tr>
<td></td>
<td>LS2</td>
<td>0.782</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>0.544</td>
</tr>
<tr>
<td>673</td>
<td>LS1</td>
<td>1.064</td>
</tr>
<tr>
<td></td>
<td>LS2</td>
<td>1.078</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>1.017</td>
</tr>
<tr>
<td>723</td>
<td>LS1</td>
<td>1.305</td>
</tr>
<tr>
<td></td>
<td>LS2</td>
<td>1.317</td>
</tr>
<tr>
<td></td>
<td>LS3</td>
<td>1.325</td>
</tr>
</tbody>
</table>
Using the Boltzmann-Matano method, the concentration dependent interdiffusion coefficients were calculated. While LS1 of the 623K couple yields a consistent Matano composition, it was excluded from subsequent analysis on account of its poor fit. The interdiffusion coefficients are presented as a function of Zn concentration in Figure 13. Compared to the Al, the interdiffusion of Zn in the Mg\textsubscript{Zn} solid solution is relatively unchanged over the composition range investigated. At the lowest temperature, the large variations in the concentration gradient made it hard to extract reliable diffusion data therefore a dashed line is shown to convey the likely profile. Again, similar to a feature seen in the Al diffusion profiles, there is an offset at about 1.5 at.% Zn. The offset is not as significant in magnitude as was seen in the Mg vs. MA9 profiles however, the origin of the offset may be the same. This phenomenon will be discussed further in Chapter 5.
The classical Boltzmann-Matano interdiffusion coefficient was transformed to a compositional independent average effective interdiffusion coefficient. Using the Arrhenius relationship, the activation energy and pre-exponential factor was calculated. However, due to the difficulty in mining dependable interdiffusion data from the 623K couple, it was not used in the determination of the pre-exponential factor and activation energy. The average effective interdiffusion coefficients, activation energy, and pre-exponential factor are presented in Table 9.

Figure 13: Mg vs. MZ6 Boltzmann-Matano interdiffusion coefficient as a function of Zn composition
Table 9: Zn average effective interdiffusion coefficients, pre-exponential factor, and activation energy

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\bar{D}^{\text{eff}}$ m²/sec</th>
<th>Individual</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>623K</td>
<td>$7.77\times10^{-16}$</td>
<td>$7.77\times10^{-16}$</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>673K</td>
<td>$2.40\times10^{-14}$</td>
<td>$2.41\times10^{-14}$</td>
<td>$1.03\times10^{-16}$</td>
<td></td>
</tr>
<tr>
<td>723K</td>
<td>$1.17\times10^{-13}$</td>
<td>$1.19\times10^{-13}$</td>
<td>$2.57\times10^{-15}$</td>
<td></td>
</tr>
</tbody>
</table>

$D_o$ (m²/sec) | 2.67x10⁻⁴ | -- |
Q (kJ/mole) | 129.5 | -- |

The pre-exponential factor and activation energy for Zn impurity diffusion in Mg was determined through graphical extrapolation of the interdiffusion coefficient, determined with the Boltzmann-Matano method. Table 10 summarizes the results of the graphical extrapolation of interdiffusion to impurity diffusion coefficients. The pre-exponential factor is found to be $1.73\times10^{-4}$ m²/sec and the activation energy for impurity diffusion is 129.8 kJ/mole. When determined through extrapolation of the Boltzmann-Matano interdiffusion coefficient profile, the activation energy for Zn impurity diffusion is unexpectedly similar to than the average effective interdiffusion activation energy, which was 129.5 kJ/mole.
Table 10: Boltzmann-Matano Zn extrapolated impurity diffusion coefficients pre-exponential factors, and activation energies

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$D_{\text{Zn}}$ m^2/sec</th>
<th>Individual</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>623K</td>
<td>2.34x10^{-15} 1.80x10^{-15}</td>
<td>2.07x10^{-15}</td>
<td>3.82x10^{-16}</td>
<td></td>
</tr>
<tr>
<td>673K</td>
<td>1.53x10^{-14} 2.13x10^{-14}</td>
<td>1.83x10^{-14}</td>
<td>4.24x10^{-15}</td>
<td></td>
</tr>
<tr>
<td>723K</td>
<td>6.79x10^{-14} 6.51x10^{-14} 6.23x10^{-14}</td>
<td>6.51x10^{-14}</td>
<td>2.80x10^{-15}</td>
<td></td>
</tr>
<tr>
<td>D_0 (m^2/sec)</td>
<td>1.73x10^{-4}</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q (kJ/mole)</td>
<td>129.8</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Given the uncertainty in the impurity diffusion coefficients extrapolated from the concentration profiles using the Boltzmann-Matano approach, the analytical Hall approach was evaluated to determine the interdiffusion coefficient for compositions less than 0.5 at. % Zn. Figure 14 displays the interdiffusion coefficient profiles using both methods. For graphical clarity, only one line scan is plotted per diffusion couple. As was seen in the Mg vs. MA9 system, there is good coherency between the two methods. The consistency of results obtained implies accuracy in the impurity diffusion coefficient obtained through the Hall method.
Figure 14: Interdiffusion in the Mg rich solid solution of the Mg-Zn binary system. The demarcation separates the analysis based on the Hall method and that based on the Boltzmann-Matano method.

Using the Hall diffusion coefficient at the infinitely dilute composition, the activation energy and pre-exponential factor of the impurity diffusion can be ascertained. Two approaches to determining the impurity diffusion coefficient for each line scan were employed. The first method uses the calculated coefficient at the lowest non-zero composition while the second method extrapolates the diffusion profile to a zero concentration. Table 11 presents the results of both methods and serves as a comparison.
between the composition minima and the extrapolated Hall results. As previously described, the Hall Method considers only the low concentration region of the concentration profile. Examination of the fitted profiles shows adequate fit for all line scans as the concentration of Zn approaches 0 at.%. Therefore, all line scans were used in the Hall analysis. The pre-exponential factor and activation energy for Zn impurity diffusion in Mg as determined from the composition minima is \(1.31 \times 10^{-5} \text{ m}^2/\text{sec}\) and 111.2 kJ/mole, respectively. Similarly, when using the extrapolated Hall method, the activation energy is 109.8 kJ/mole and the pre-exponential factor is \(1.03 \times 10^{-5} \text{ m}^2/\text{sec}\). Regardless of the approach in extracting the impurity diffusion coefficient using the Hall Method, the results yield substantially different results than the graphical extrapolation of the Boltzmann-Matano method. The activation energy for Zn impurity diffusion is lower than the average effective interdiffusion activation energy, which was 129.5 kJ/mole. The analytical solution confirms the activation energy for Zn impurity diffusion is lower than the activation energy for interdiffusion.
Table 11: Hall Zn impurity diffusion coefficients pre-exponential factors, and activation energies

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Composition Minima</th>
<th>Extrapolation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{Zn}^*$ (m$^2$/sec)</td>
<td>$D_{Zn}^*$ (m$^2$/sec)</td>
</tr>
<tr>
<td></td>
<td>Individual</td>
<td>Average</td>
</tr>
<tr>
<td>623</td>
<td>5.57x10^{-15}</td>
<td>3.36x10^{-15}</td>
</tr>
<tr>
<td>673</td>
<td>4.78x10^{-14}</td>
<td>6.48x10^{-14}</td>
</tr>
<tr>
<td>723</td>
<td>9.05x10^{-14}</td>
<td>8.23x10^{-14}</td>
</tr>
<tr>
<td>$D_o$ (m$^2$/sec)</td>
<td>1.31x10^{-5}</td>
<td>--</td>
</tr>
<tr>
<td>Q (kJ/mole)</td>
<td>111.2</td>
<td>--</td>
</tr>
</tbody>
</table>
CHAPTER 5: DISCUSSION

Table 12 provides, for the readers’ convenience, a summary of the various diffusion coefficients, pre-exponential factors, and activation energy as determined in this study. The diffusion coefficients determine by Hall analytical method were extrapolated to a zero concentration to yield the impurity diffusion coefficients. The average effective interdiffusion coefficients are valid over the composition range specified in the table.

Table 12: Comparison of pre-exponential factor and activation energy for diffusion in Mg(ss).

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Diffusion Coefficient</th>
<th>Pre-exponential factor, $D_0$ (m$^2$/sec)</th>
<th>Activation Energy, $Q$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al</td>
<td>Hall Analytical</td>
<td>Impurity Diffusion, $D^*$ (m$^2$/sec) (extrapolated)</td>
<td>1.61x10^{-4}</td>
<td>144.1</td>
</tr>
<tr>
<td></td>
<td>Boltzmann-Matano</td>
<td>Effective Interdiffusion, $\bar{D}^{eff}$ (m$^2$/sec) (0-8.5 at.% Al)</td>
<td>7.69x10^{-1}</td>
<td>186.8</td>
</tr>
<tr>
<td>Mg-Zn</td>
<td>Hall Analytical</td>
<td>Impurity Diffusion, $D^*$ (m$^2$/sec) (extrapolated)</td>
<td>1.03x10^{-5}</td>
<td>109.8</td>
</tr>
<tr>
<td></td>
<td>Boltzmann-Matano</td>
<td>Effective Interdiffusion, $\bar{D}^{eff}$ (m$^2$/sec) (0-2.0 at.% Zn)</td>
<td>2.67x10^{-4}</td>
<td>129.5</td>
</tr>
</tbody>
</table>

5.1 Interdiffusion

The interdiffusion of Mg-Al solid solution increases with increasing Al concentration as shown in Figure 11. This is intuitively consistent with predictions based on the phase
diagram, shown in Figure 15, and equilibrium vacancy concentration described in §2.1. As the Al concentration increases, the solidus and liquidus of Mg solid solution decrease. Therefore, at any given isothermal anneal temperature the concentration of vacancies will increase with increasing Al concentration. The interdiffusion coefficients increased by an order of magnitude with increase in Al concentration.

To a greater extent than seen the Mg$_{Al}$ solid solution, the melting point decreases with increasing solute concentration in the Mg$_{Zn}$ solid solution. From the Mg-Zn phase diagram presented in Figure 16, the slope of the Mg$_{Zn}$ solid solution solidus is nearly 5 times as steep as the solidus for Mg$_{Al}$ solid solution. While it may be tempting to draw a direct relationship from vacancy concentration to diffusivity as implied for the Mg$_{Al}$ solid solution, if the mere presence of vacancies facilitated diffusion the interdiffusion of Mg$_{Zn}$ solid solution would show strong concentration dependence. However this is not the case, as shown in Figure 13. The interdiffusion profile remains relatively constant across the compositional spectrum.
Figure 15: Al-Mg phase diagram (Okomoto, 1998)
A common feature in the interdiffusion profiles of the two systems studied is a positive offset. In the Mg_{Al} solid solution, the uptick occurs just above 6.5 at.% Al while in the Mg_{Zn} solid solution, the uptick is present as Zn concentration approaches 1.5 at.%.

The increase in the interdiffusion coefficients at the noted compositions may indicate a shift of dominating diffusion mechanisms, be a consequence of experimental technique, or be an artifact of the curve fitting protocol.

In both systems, the composition of the alloys used in this study is near the solubility limit of the solute atoms in the Mg solid solution. There may be competing
attractions for the solute atoms as the composition approaches the solid solubility solvus. As the solute concentration increases, lattice strain increases. The offset may signify a critical lattice strain which affects the thermodynamics of the local atomic environment.

It is possible that the uptick is a consequence of precipitate dissolution. While the diffusion anneals are done in the solid-solution regime, the alloys exist in a two-phase equilibrium at room temperature. No special precautions were taken to preclude natural aging and microstructural characterization was not performed prior to diffusion anneals.

Finally, the curve fitting protocols relied on smoothing of the defining splines as described in §3.5. A satisfactory fit cannot be achieved with cubic splines if additional points beyond the terminal ends are not collected because of the tendency of polynomials to develop fluctuations in these regions. Similarly, a satisfactory fit may require the junctions or nodes between the piecewise functions to be non-uniformly incremented to prevent fluctuations within the profile (Kapoor & Eagar, 1990). The smoothing factors implemented in this study were intended to compensate for fit instabilities.

5.2 Average Effective Interdiffusion

The average effective interdiffusion coefficient was calculated for each couple and presented in Table 5 and Table 9. The average effective interdiffusion coefficient for MgAl solid solution is plotted in Figure 17 alongside interdiffusion results experimentally determined by other researchers as a function of temperature (Brennan, Bermudez, Kulkarni, & Sohn, Interdiffusion in the Mg-Al system and intrinsic diffusion in Mg2Al3, 2012), (Moreau, 1971). There is good agreement with recently published work by Brennan.
while the activation energy appears to be higher than that which was determined by Moreau. However, close examination of Moreau's publication revealed a relatively large variation in activation energy – he reported 143.6 ± 10.9 kJ/mole (Moreau, 1971). Furthermore, Moreau's average interdiffusion pre-exponential factor and activation energy are reportedly valid over the compositional range of 0-20 at.% Al, well beyond the solubility limit of Al in Mg which is 12 at.% Al. Therefore the average interdiffusion data presented by Moreau cannot be considered meaningful for comparison with the present work.

Figure 18 presents the average effective interdiffusion results for MgZn solid solution. However since no experimental interdiffusion data for Zn in Mg solid solution could be found in literature, Zn tracer diffusion coefficient in Mg is included for comparison. As described, the average effective interdiffusion coefficient for the 623K couple was not used in the calculation of the activation energy or pre-exponential factor for the interdiffusion coefficient of MgZn solid solution. A dashed line is used to show the uncertainty at 1.6K⁻¹ (623K). Additional diffusion studies are required to confirm the expected average effective interdiffusion coefficient at 623K. Nonetheless, there is very good agreement between the results of this study and those determined by Čermák.
Figure 17: Average effective interdiffusion of Mg$_{Al}$ solid solution as a function of temperature. Open markers represent effective interdiffusion coefficient of each line scan. (Brennan, Bermudez, Kulkarni, & Sohn, Interdiffusion in the Mg-Al system and intrinsic diffusion in Mg$_2$Al$_3$, 2012) (Moreau, 1971)
Figure 18: Average effective interdiffusion of Mg\textsubscript{Zn} solid solution as a function of temperature. Open markers represent effective interdiffusion coefficient of each line scan. (Čermák & Stoukal, 2006)

There is an obvious difference in the activation energy and pre-exponential factor for average effective interdiffusion coefficients for the two solid solutions. The activation energy for the Mg\textsubscript{Al} solid solution is roughly 50% higher than the activation energy for the Mg\textsubscript{Zn} solid solution. This means that an Al atom has a larger barrier it must overcome before it can move to a neighboring position. In consideration of diffusion mechanisms previously described, even if the atom achieves sufficient energy to overcome the activation barrier, there is a probability an adjacent position will not be available. Thus, the
activation energy is a measure of the probability of successful jump. The pre-exponential factor is a cumulative term which represents, in part, the correlation of jumps and entropy of attempts (Balluffi, Allen, & Carter, 2005). As atomic jump correlation increases the correlation term in the pre-exponential factor approaches unity. The pre-exponential factor for MgZn solid solution is significantly lower than that for MgAl solid solution suggesting highly correlated jumps in MgAl solid solution. The logical interpretation of the average interdiffusion coefficients is that interdiffusion occurs more readily in MgZn than MgAl solid solutions.

5.3 Impurity Diffusion

The impurity diffusion coefficient was calculated for each couple using the Hall analytical method. The diffusivity of Al impurities in Mg solid solution is plotted as a function of temperature in Figure 19. Al impurity diffusion data measured by Brennan using thin film techniques and data calculated by Ganeshan using the 8-frequency model is also included. The experimental data published prior to this study has been acknowledged by the researcher that the refined microstructure and depth profiling methodology employed resulted in a broadening of the diffusion profile which led to somewhat inflated diffusion coefficients (Brennan, et al., Aluminum Impurity Diffusion in Magnesium, 2012). Thus, as expected, the Al impurity diffusion coefficients established in this study are slightly lower than previously published. The activation energy for Al impurity diffusion in Mg as determined by the Hall analytical method has very good agreement with the first-principles activation energy. On the other hand, the pre-exponential factor differs by an
order of magnitude. This phenomenon can be rationalized by considering the previously
described diffusion mechanisms. First principles calculations are carried under the
presumption of single crystal geometry. This study utilized metals which, by their very
nature of being polycrystalline, have a higher concentration of defects thereby increasing
atomic mobility. Therefore, it is not unexpected to see the diffusion coefficients
experimentally determined in this study to be an order of magnitude higher that the
computationally established values.
The Zn impurity diffusion coefficient as a function of temperature is presented in Figure 20. The comparative Zn impurity diffusion data was determined by Čermák and Lal through tracer diffusion experiments and summarized by Neumann as described in §2.5. Zn impurity data calculated by Ganeshan based on first principles modeling is also graphically reported. There is good agreement between the impurity diffusion coefficients experimentally revealed but the activation energy has been found to be slightly lower in this study. A contributing factor in this disparity appears to be an elevated average
diffusion coefficient for the couple annealed at 673K. The Arrhenius relationship was determined from the average diffusion coefficient at each temperature rather than individual data points. As can be seen, the data points for the 623K and 723K couples fall directly in line with the published tracer diffusion data. The congruency in results between the isotopic tracer diffusion coefficient and the impurity diffusion coefficient lends credence to the analytical method presented herein.

Figure 20: Zn impurity diffusion in Mg solid solution as a function of temperature. (Neumann & Tuijn, 2009) (Ganeshan, Hector Jr., & Liu, 2011)
In order to uncover trends for impurity diffusion in Mg, the impurity coefficients of diffusion for various elements have been plotted in Figure 21. As is customary, tracer diffusion studies were performed in the determination of Mg self-diffusion coefficients and impurity diffusion coefficients for In and Fe (Pavlinov, Gladyshev, & Bykov, 1968). The impurity diffusion coefficients for Ce and La were analytically determined by assuming the diffusivity to be constant and measuring the rate of precipitate dissolution (Lal, 1967). On the other hand, the impurity diffusion coefficient of Be in Mg was determined through solid-to-solid diffusion couples (Yerko, Zelenskiy, & Krasnorutskiy, 1966).

Because Al is mono-isotopic, In has been used as a substitute for Al in diffusion studies. The primary reason for this substitution is that In diffuses in Al at the same rate as Al self-diffusion (Eggersmann & Mehrer, 2000). However, examination of Figure 21 provides a clear indication that In impurities diffuses faster than Al impurities in Mg, in particular at lower temperatures. The kinetic behavior of Be impurities, on the other hand, appears to be similar to that of Al impurities in Mg. Additionally, the Mg self-diffusion coefficient as a function of temperature is included for comparison.

Further consideration of Figure 21 reveals Zn impurity diffusion to be faster than Mg self-diffusion which, in turn, is faster than the Al impurity diffusion. These empirical findings are in conflict with the conclusions from 8-frequency modeling which found Mg to self-diffuse faster than both Al and Zn impurities (Ganeshan, Hector Jr., & Liu, 2011). One possible atomistic explanation for fast diffusion of Zn in Mg may be related to the small atomic radius of Zn in comparison to that of Mg. It is possible that Zn solutes have a small
interstitial component with high mobility in Mg as has been seen in the Au/Pb system (Mehrer, 2007). In such a case, the Zn substitutional atom, having an atomic size ratio to Mg atoms of 0.84, may move by the dissociative mechanism described in §2.1. The first principles calculations were based on the assumption that diffusion was vacancy mediated (Ganeshan, Hector Jr., & Liu, 2011).

The empirical finding can be further rationalized by considering the thermodynamics of diffusion. The driving force for diffusion was defined in Chapter 2 as the gradient of chemical potential. The chemical potential is the molar free energy resulting from the dilution of solute atoms and it is dependent on the activity of the solution. The activity of a solute in a condensed solution is the ratio of its partial pressure to its saturated vapor pressure (Gaskell, 2003). Therefore, the diffusion coefficient is proportional to the vapor pressure of the solutes. The vapor pressure of Al, Mg, and Zn at the diffusion anneal temperatures are listed in Table 13. The values are calculated using the Riedel equation (Vetere, 1991). The saturated vapor pressure of Zn is notably higher than that of Al and marginally higher than that of Mg. On this basis, the observations of $D_{Zn}^* > D_{Mg}^* > D_{Al}^*$ is founded.

Table 13: Saturated vapor pressure of Al, Mg, and Zn at the diffusion anneal temperatures (Alcock, Itkin, & Horrigan, 1984)

<table>
<thead>
<tr>
<th>(atm)</th>
<th>Al</th>
<th>Mg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>623K</td>
<td>2.6x10^{-21}</td>
<td>4.4x10^{-7}</td>
<td>1.7x10^{-5}</td>
</tr>
<tr>
<td>673K</td>
<td>2.8x10^{-19}</td>
<td>3.5x10^{-6}</td>
<td>1.1x10^{-4}</td>
</tr>
<tr>
<td>723K</td>
<td>1.6x10^{-17}</td>
<td>2.1x10^{-5}</td>
<td>5.4x10^{-4}</td>
</tr>
</tbody>
</table>
5.4 Impurity vs. Tracer Diffusion Coefficients

As described in Equation (10), interdiffusion can be related to impurity diffusion through incorporation of the thermodynamic factor, $\Phi$, and vacancy wind factor, $S$. In a solid solution, the vacancy wind factor will remain virtually constant near unity (Belova & Murch, 2001). In Mg$_2$Al solid solution, the thermodynamic factor increases slightly from
1.0<\Phi<1.1 with increasing solute concentration for the temperatures studied; in the Mg\textsubscript{Zn} solid solution, the thermodynamic factor decreases slightly from 1.0>\Phi>0.9 with increasing solute concentration (Zhou & Liu, 2013). A fundamental assumption of this study has been that the impurity diffusion coefficient in Mg is equivalent to the tracer diffusion coefficient throughout the compositional range. Therefore, examination of relationship between the interdiffusion coefficients determined through Boltzmann-Matano analysis and the impurity diffusion coefficients determined through the Hall analysis and published self-diffusion coefficients gives some insight into the behavior of the tracer diffusion coefficient. The impurity diffusion coefficient is determined to be valid only in the infinitely dilute solutions and the tracer diffusion coefficient varies as a function of composition.

5.5 Hall Analytical Method

Since, the Boltzmann-Matano method for determining the interdiffusion coefficient as a function of concentration relies on the slope of the diffusion profile and the balance of the areas between the profile and Matano interface, uncertainty in the raw data can yield uncertain results. In consideration of the Zn impurity diffusion results presented herein, the extracted impurity diffusion coefficients using the Hall analysis of solid-to-solid diffusion couples compare well to the conventional isotopic tracer diffusion studies. However, this method also has limitations. The concentration profile is expected to conform to the probability density function which has an error function solution. Not all concentration profiles satisfy the error function in its entirety. Therefore, the validity of the Hall method is limited to the region of either low or high concentration and is not
applicable at intermediate concentrations. Figure 22 provides a stacked plot with a fit concentration profile and an example of the corresponding semi-probability plot of the concentration distribution against the Boltzmann variable, η. The linear regression line is shown on the semi-probability plot.

Figure 22: Fit concentration profile stacked with the corresponding semi-probability plot of the concentration distribution vs. the Boltzmann variable.

In order to calculate the value of u as described in §2.2.4.1, the inverse of the standard normal cumulative distribution function must be calculated at each concentration probability. The conversion $C/C_\infty$ to a Z-score is an iterative process which can introduce
error. The Z-score is the upper bound of the cumulative distribution function and is proportional to the \( u \) parameter. The \( u \) parameter is a straight line at the compositional extremes when plotted against the Boltzmann variable. The slope and intercept of this straight line are determined with a least squares linear regression model and used in the diffusion formula presented in Equation (11). The linear regression, by definition, carries a degree of error; the distance between any point and the regression line points represent the error. The objective of a least squares regression is to minimize the random error term (Mendenhall & Sincich, 2007). Regression model inputs, such as the number of points to include in the linear regression, can affect the slope and intercept of the fit. Similarly, the least squares linear regression model is based on the assumption that the errors associated with two different observations are independent (Mendenhall & Sincich, 2007); this assumption may be violated in the curve fitting process. Despite these limitations, the analytical approach has proven to be an effective tool for calculating impurity diffusion coefficients.
CHAPTER 6: SUMMARY AND CONCLUSIONS

The objective of this thesis was two-fold: first, was the examination of interdiffusion in the Mg solid solution phase of the binary Mg-Al and Mg-Zn systems; second, was to explore non-conventional analytical methods to determine impurity diffusion coefficients. The diffusion behavior in the Mg solid solution of the binary Mg-Al and Mg-Zn systems was examined in the temperature range of 623 – 723K using solid-to-solid diffusion couples. The quality of diffusion bonding was evaluated by optical microscopy and scanning electron microscopy with X-ray energy dispersive spectroscopy, and concentration profiles were determined using electron probe microanalysis with pure standards and ZAF matrix correction.

Interdiffusion coefficients were calculated using the Boltzmann-Matano analysis as were average effective interdiffusion coefficients. The interdiffusion of MgAl solid solution increases with increasing Al concentration and a notable uptick occurs at approximately 6.5 at.% Al. Activation energy and pre-exponential factor for the average effective interdiffusion coefficient in MgAl solid solution was determined to be 186.8 KJ/mole and 7.69 x 10^{-1} m^2/sec. On the other hand, the interdiffusion profile remains relatively constant across the compositional spectrum of MgZn solid solution. For the MgZn solid solution, interdiffusion coefficients did not vary significantly as a function of Zn concentration, however an offset was observed as the concentration approached 1.5 at.% Zn. Activation energy and pre-exponential factor for the average effective interdiffusion coefficient in MgZn solid solution was determined to be 129.5 KJ/mole and 2.67 x 10^{-4} m^2/sec. The logical
interpretation of the average interdiffusion coefficients is that interdiffusion occurs more readily in Mg<sub>Zn</sub> than Mg<sub>Al</sub> solid solutions. The offset in the interdiffusion coefficient profile at the noted compositions may indicate a shift of dominating diffusion mechanisms, be a consequence of experimental technique, or be an artifact of the curve fitting protocol.

As the concentration of Al or Zn approaches the dilute ends, a non-conventional approach was taken to estimate the impurity diffusion coefficients. The Hall analytical method for extracting impurity diffusion coefficients from solid-to-solid diffusion couple studies has proven to be effective and yields comparable results to those obtained through conventional isotopic tracer diffusion studies. This method was validated by comparing outcomes obtained in this study through solid-to-solid diffusion couples with results established through conventional impurity diffusion studies using isotopic tracers.

Impurity diffusion coefficients of Al in Mg was determined to have activation energy and pre-exponential factor of 144.1 KJ/mole and 1.61 x 10<sup>-4</sup> m<sup>2</sup>/sec. Impurity diffusion coefficients of Zn in Mg was determined to have a activation energy and pre-exponential factor of 109.8 KJ/mole and 1.03 x 10<sup>-5</sup> m<sup>2</sup>/sec. Zn impurity diffusion is faster than Mg self-diffusion which, in turn, is faster than the Al impurity diffusion.
APPENDIX A: MG VS. MA9 CONCENTRATION PROFILES
This appendix provides the EPMA data for each line scan (LS) performed on the Mg vs. MA9 diffusion couples, represented by open circle markers. The fitted concentration profiles, when applicable, are represented by a solid line and have been superimposed over the EPMA data.

Figure 23: Lines scan #1 of Mg vs. MA9, annealed for 96 hrs. at 623K
Figure 24: Lines scan #2 of Mg vs. MA9, annealed for 96 hrs. at 623K
Figure 25: Lines scan #3 of Mg vs. MA9, annealed for 96 hrs. at 623K
Figure 26: Lines scan #1 of Mg vs. MA9, annealed for 17 hrs. at 673K
Figure 27: Lines scan #2 of Mg vs. MA9, annealed for 17 hrs. at 673K
Figure 28: Lines scan #3 of Mg vs. MA9, annealed for 17 hrs. at 673K
Figure 29: Lines scan #1 of Mg vs. MA9, annealed for 24 hrs. at 723K
Figure 30: Lines scan #2 of Mg vs. MA9, annealed for 24 hrs. at 723K
Figure 31: Lines scan #3 of Mg vs. MA9, annealed for 24 hrs. at 723K
APPENDIX B: MG VS. MZ6 CONCENTRATION PROFILES
This appendix provides the EPMA data, represented by open circle markers, for each line scan (LS) performed on the Mg vs. MZ6 diffusion couples. The fitted concentration profiles, when applicable, are represented by a solid line and have been superimposed over the EPMA data.

Figure 32: Lines scan #1 of Mg vs. MZ6, annealed for 48 hrs. at 623K
Figure 33: Lines scan #2 of Mg vs. MZ6, annealed for 48 hrs. at 623K
Figure 34: Lines scan #3 of Mg vs. MZ6, annealed for 48 hrs. at 623K
Figure 35: Lines scan #1 of Mg vs. MZ6, annealed for 8 hrs. at 673K
Figure 36: Lines scan #2 of Mg vs. MZ6, annealed for 8 hrs. at 673K
Figure 37: Lines scan #3 of Mg vs. MZ6, annealed for 8 hrs. at 673K
Figure 38: Lines scan #1 of Mg vs. MZ6, annealed for 24 hrs. at 723K
Figure 39: Lines scan #2 of Mg vs. MZ6, annealed for 24 hrs. at 723K.
Figure 40: Lines scan #3 of Mg vs. MZ6, annealed for 24 hrs. at 723K
LIST OF REFERENCES


