Interdiffusion Study Of Mg-aa6061 System

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INTERDIFFUSION STUDY OF MG-AA6061 SYSTEM

by

MIAN FU
B.S. Shandong University, 2011

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 Orlando, Florida

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ABSTRACT

Magnesium (Mg) is a light-weight metal that has extraordinary physical and chemical properties for many potential applications in automobile, military, and electronics. Aluminum alloys, because of its light-weight, high strength and corrosion resistance have a wide range of commercial applications. Given these two, sometime competing, alloy systems, there are now many applications where the metallurgical compatibility of Mg- and Al-alloys are required for engineering applications. One such case is the development of diffusion barrier for U-Mo metallic fuel in Al-alloy cladding, where Mg, with its complete immiscibility with U and Mo is being considered as the diffusion barrier. While negligible diffusional interaction between Mg and U-Mo alloys have been reported, diffusional interaction between the Mg and Al-alloy cladding has not been investigated.

In this study, solid-to-solid diffusion couples were assembled using discs of pure Mg (99.999 %) and AA6061 Al-alloy. After preparation, Mg was diffusion bonded to AA6061 in sealed quartz capsule at 300°, 350°, and 400°C for 720, 360, and 240 hours, respectively. Scanning electron microscopy was used to inspect the interdiffusion zone, while phase identification was performed using X-ray energy dispersive spectroscopy. One specific phase that exists in the binary Mg-Al system, labeled “ε” was observed and characterized by transmission electron microscopy. From the preceding data, the growth rates as well as interdiffusion coefficients of the intermetallic phases were extracted and compared to previous investigations using pure Mg and Al.
I dedicate this paper to my parents. Your love will never die.
ACKNOWLEDGMENTS

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I appreciate Dr. Kevin Coffey for providing the financial means and the entrance chance to United States, to UCF, which have allowed me to pursue my graduate degrees. I am grateful for the colloquies with Dr. Linan An through which he stretched my thinking and enlightened me in so many ways. I am honored to have these fine gentlemen serve on my
thesis committee.
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LIST OF ACRONYMS

η    Boltzmann variable
AA   Aluminum Alloy
Al   Aluminum
at.% Atomic percent
Au   Gold
BSE  Back-scattered electrons
Ci   Concentration of component i
Co   Concentration of component i at Matano plane
CR,L Concentration of component i at terminal end
D    Diffusion Coefficient (m²/sec)
Do   Pre-exponential factor (m²/sec)
D̃    Binary interdiffusion coefficient (m²/sec)
Deff  Average effective interdiffusion coefficient (m²/sec)
XEDS Energy Dispersive Spectroscopy
Fe   Iron
HCP  Hexagonal Close Packed crystal structure
I    Interstitial solvent atom
Ji   Diffusion flux of component I (mole·m⁻²·sec⁻¹)
J̇    Interdiffusion flux (mole·m⁻²·sec⁻¹)
Mo  Molybdenum
Mg  Magnesium

n_i  Mole fraction of component i

Pb  Lead
Pu  Plutonium

Q  Activation energy (kJ/mole)
R  Ideal gas constant (8.314772 kJ/mole)

SE  Secondary Electrons

t  Time (seconds)

T  Temperature (Kelvin)

U  Uranium

wt.%  Weight percent

x  Position (µm)

x_o  Matano plane position

XEDS  X-ray Energy Dispersive Spectroscopy

Z  Atomic number

Zr  Zirconium
CHAPTER 1: INTRODUCTION

Depleted Uranium-Molybdenum (U-Mo) alloy is an important nuclear fuel being developed for use in research and test reactors because of its excellent characteristics, such as being easily reprocessed and remotely refabricated, and its inherent proliferation-resistance.[1] As a result, low-enrichment U-Mo dispersion and monolithic fuels encased in Aluminum (Al) alloys are developed for the Reduced Enrichment for Research and Test Reactor (RERTR) Program.[2-4] While the exact configuration of the fuel plate can vary in structure and composition, two fundamental arrangements can describe the structural design of the plates. In one design, U-Mo particulates are dispersed in an aluminum alloy matrix. The other convention is a monolithic U-Mo foil clad with aluminum alloy sheet or plate.[5] Figure 1 shows the schematics of these two structures. The fuel typically contains 10 wt. % Mo while the cladding or matrix is usually 6061 aluminum alloy.

![Figure 1: Schematics of (a) dispersion and (b) monolithic U-Mo alloy fuel configuration][5]
However, during processing and irradiation metallurgical interactions can and do occur between the fuel and Al alloy encasement due to interdiffusion.[6, 7] Diffusion reaction products of aluminides are detrimental to the system primarily because they have lower thermal conductivities and greater thermal expansion raising the fuel operating temperature and inducing destructive stresses, respectively.

In order to prevent these interdiffusion reactions, different approaches have been proposed. For monolithic fuel plate design, barrier materials can be inserted between the U-Mo fuel and the Al alloy cladding, while for dispersion fuel plate design, substitution of the Al matrix with a non-reacting matrix is considered. Different diffusion barrier materials have been explored in several studies.[6-8] Specifically, the interdiffusion of the U-Mo fuel and Mg, Mo, Nb, and Zr barrier materials were studied. Among all of the above elements, Zr has become the standard to which other barrier materials are compared despite the formation of several reaction products[9]. Mg, on the other hand, has shown promise as a barrier material. Recent work by Huang [10] indicates that there is insignificant interdiffusion between Mg and U-Mo yet still acceptable interfacial bonding can be achieved. His findings are consistent with the expectation based on the immiscibility of Mg in both U and Mo. Furthermore, Mg has the a lower neutron absorption rate (0.063 barn) compared to that of Zr (0.185 barn).[11].

Conversely, diffusion reactions occur between Mg and Al and result in the formation of
several intermediate phases. Diffusion studies between pure Mg and pure Al have been extensively carried out [12] but little work has been to understand interdiffusion between Mg and AA6061. Researchers at Argonne National Laboratory fabricated fuel plates in which the U-Mo fuel particles were dispersed in a Mg matrix and then clad in AA6061. They qualitatively reported that subsequent processing at 415°C resulted in a reaction between the matrix and cladding yet, when the processing temperature was reduced to 275°C, no reaction occurred.[1]

In order to clarify the applicability of Mg as a barrier layer in nuclear fuel applications, it is necessary to develop a quantitative understanding of the interactions between Mg and AA6061. In this study, solid-to-solid diffusion couples were assembled and subjected to diffusion anneals at 400°, 350°, 300°C, for 240, 360, 720 hours, respectively. Scanning electron microscopy was used to inspect the interdiffusion zone, while phase identification was performed using X-ray energy dispersive spectroscopy(XEDS). One specific phase that exists in the binary Mg-Al system, labeled “ε” was observed and characterized by transmission electron microscopy. From the characterization results, the growth rates as well as interdiffusion coefficients of the intermetallic phases were extracted and compared to previous investigations using pure Mg and Al.
Solid-state diffusion science began in the nineteenth century. Without a full understanding, people used diffusion phenomena in many fields through the ages for applications such as hardened iron swords and gilded bronze wares. Lots of phenomena are related to diffusion, such as the dissipation of ink drops in water. In this situation, diffusion is caused by Brownian motion of atoms or molecules; their migration through the liquid constitutes the classic example of liquid self-diffusion. Solid-to-solid diffusion was not accepted until the nineteenth century.[13] The main reason for the lack of acceptance was the source of sufficient energy necessary to squeeze atoms through crystal lattice structures was inconceivable. Nonetheless, solid-to-solid diffusion has become fundamental in physics, chemistry, biology, and materials science.

The first systematic and quantitative studies of diffusion in gases were performed by Thomas Graham who was a chemist. Thomas Graham began the quantitative study of diffusion in gases, giving Equation 1

\[
\frac{v_A}{v_B} = \sqrt{\frac{M_B}{M_A}}
\]  

where \(v_A\) and \(v_B\) denote mean atomic velocities and \(M_A\) and \(M_B\) represent the molar mass of A.
and B molecules. Graham’s study was further developed by Maxwell and Clausius.

A great advance in the diffusion field came from the work done by Adolf Eugen Fick. Inspired by Graham’s study, Fick developed a mathematical framework for diffusion phenomena using the analogy between Fourier’s law of thermal conduction and diffusion.[13] In Fick’s first law, he postulated that the flux of matter, \( J \), in the x direction is proportional to the pertaining gradient of concentration, \( C \), described by Equation 2, where \( D \) is the diffusion coefficient or diffusivity.

\[
J = -D \frac{\partial C}{\partial x} \quad (2)
\]

However, this relationship only holds true in steady-state conditions. In consideration of nonsteady-state conditions, Fick derived the second law of diffusion given in Equation 3

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)
\]

Fick’s first law and second laws are fundamental to the study of diffusion study.

Shortly after Fick’s derivation, a metallurgist named Sir William Roberts-Austen conducted a series of studies about the impurity effects on the physical properties of pure metals and alloys focusing on the diffusion study of gold, platinum and rhodium in liquid lead. Austen extended his study to gold diffusion in solid lead. In this experiment, thin plates
of gold were fused on to the end of cylindrical Pb rods, the diameter and length of the lead rod varies based on the time and temperature of the experiment. He measured the diffusion depth of gold in lead and calculated the relative diffusivity of gold. This approach is remarkably similar to the modern solid-to-solid diffusion couple technique. Roberts-Austen observed changes in diffusivity with change in temperature and suggested a temperature dependence of the diffusion coefficient. However, he did not investigate the relationship further. But this dependency didn’t go unnoticed for long. Svante Arrhenius observed the association and formulated the relationship between temperature and the diffusion coefficient in solids in terms of activation energy. Hence the Arrhenius relationship is given in Equation 4:

\[ D = D^0 \exp \left( -\frac{Q_D}{RT} \right) \]  

(4)

In this equation, \( T \) is absolute temperature in Kelvin, \( R \) is ideal gas constant, \( Q_D \) is the activation energy of diffusion.

In terms of the diffusion controlled growth of a phase with a semi-infinite binary system, the thickness during annealing of the growing phase after time \( t \), can be described as following Equation 5 [14]

\[ k_p = \frac{x^2}{2t} \]  

(5)
Here \( x \) is the thickness measured according to the SEM microstructure of each intermetallic phase; \( k_p \) is the so called parabolic growth constant. \( t \) is the diffusion time in seconds. The temperature dependence of the parabolic growth rate constant can be determined according to Arrhenius relation Equation 6:

\[
k_p = k_0 \exp \left( -\frac{Q_k}{RT} \right)
\]

Again, \( T \) is annealing temperature and \( R \) is ideal gas constant, however \( Q_k \) is activation energy of the growth reaction.

Ludwig Boltzmann published a paper in 1894 which mathematically treated Fick’s nonlinear partial differential equation for the case of composition dependent diffusivity. By introducing a new variable, given in Equation 7, Boltzmann was able to transform Fick’s second law into a nonlinear second order ordinary differential equation. The resulting equation is known as the Boltzmann Transformation and reflected in Equation 8

\[
\eta = \frac{x}{2\sqrt{t}}
\]

\[
-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta} \left( D(C) \frac{dC}{d\eta} \right)
\]
In the 1940s, an American metallurgist Ernest Kirkendall and his coworkers observed a shift in position of inert markers from the original interface in their Cu-Brass diffusion couple study. This marker plane movement was termed the Kirkendall effect. The discovery of the Kirkendall effect marked a new cornerstone of solid to solid diffusion.[13]

2.2 Types of Diffusion Coefficients

There are several different types of diffusion coefficients, each of which has a different meaning and derivation. Technologically relevant coefficients of diffusion include the following:

- Interdiffusion coefficient
- Average effective interdiffusion coefficient
- Intrinsic diffusion coefficient
- Impurity diffusion coefficient
- Tracer diffusion coefficient

In interdiffusion, atoms move because of the concentration varies in different positions therefore the interdiffusion coefficient is descriptive at a specific composition only. Average effective interdiffusion coefficient provides a single nominal coefficient for the compositional spectrum. The intrinsic diffusion coefficient, $D_i$, describes diffusion of the
individual components relative to the lattice planes. Impurity diffusion is the motion of dilute solutes while tracer diffusion is the migration of an isotope the naturally occurring state.

In this study, interdiffusion coefficient and average effective interdiffusion coefficient are used to analyze the interdiffusion behavior. To better explain these two coefficients, following are some details about them.

2.2.1 Interdiffusion

Interdiffusion also refers to chemical diffusion. The chemical composition varies with changing of position \( x \). As a result, the diffusioning atoms experience variable environments in terms of chemical potential. This, in turn, can result in a composition dependence of the interdiffusion coefficient. The interdiffusion process is graphically shown in Figure 2.

![Figure 2: Schematic of interdiffusion process where \( t_0 < t_1 < t_2 \). The concentration profile shows the concentration of A across the diffusion zone.](image)
Thus, Fick’s Second Law for interdiffusion in the x direction can be written as Equation 9:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( \bar{D}_i \frac{\partial c_i}{\partial x} \right) = \bar{D}_i \frac{\partial^2 c_i}{\partial x^2} + \frac{d \bar{D}_i}{d c_i} \left( \frac{\partial c_i}{\partial x} \right)^2$$  \hspace{1cm} (9)$$

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 Equation 10:

$$\frac{\partial c}{\partial t} = \bar{D}_{(c)} \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (10)$$

In binary systems, diffusivity can be determined from concentration profiles using the Boltzmann-Matano method, under the presumption of constant molar volume, when the molar volume substantially changes other approaches, to solving the diffusion equation must be employed. The Boltzmann-Matano method applies boundary conditions to the Boltzmann transformation and relies on the precise determination of the Matano plane. The Matano plane, $x_o$, is located by balancing the mass of the diffusing atoms. Mathematically, it is determined by the integrating the concentration profile such that the condition of Equation 11 is satisfied.

$$\int_{c^0}^{c^R} x dC + \int_{c^0}^{c_o} x dC = 0$$  \hspace{1cm} (11)$$
The composition at the Matano Plane is $C^0$, the composition at the terminal ends of the couple is $C^L$ and $C^R$.

The interdiffusion flux of component, $\bar{J}_i$, can be calculated using as shown in Equation 12

$$\bar{J} = \frac{1}{2t} \int_{C^z}^{C(x)} (x - x_o) \, dC$$ \hspace{1cm} (12)

The interdiffusion coefficient, $\bar{D}_c$, can then be calculated rearranging Fick’s first law, given in Equation 2 and substituting in the interdiffusion flux shown in Figure 14, gives Equation 13

$$\bar{D}_c = -\frac{\frac{1}{2t} \int_{C_i}^{C_i(0)} (x=x_o) \, dC_i}{\frac{\partial C_i}{\partial x}}$$ \hspace{1cm} (13)

The Sauer-Freise Method can be used when changes in molar volume, Vm, occur as in the case of multicomponent diffusion reactions, The molar volume of a phase can be calculated by dividing the density of the phase, found on x-ray diffraction JCPDS cards, into the average molar mass, The molar volume of Mg solid solution is 14 cm$^3$/mol while the molar volume of Al solid solution is 10 cm$^3$/mol. Vegard’s rule suggests a linear relationship between molar volume and mole fraction. Nonideal solutions, however, deviate from this rule. Specifically, the
molar volume of $\gamma$-Mg$_{17}$Al$_{12}$ is 12.2 cm$^3$/mol whereas Vegard’s would suggest a molar volume of 11.7 cm$^3$/mol. The molar volume of $\beta$-Mg$_2$Al$_3$ is 11.6 cm$^3$/mol which is as predicted by Vegard’s rule. This subtle positive deviation may be significant enough to warrant use of the Sauer-Freise method. This method essentially normalizes the concentration and the diffusion is modified as shown in Equation 14

$$
\bar{D}(Y^*) = \frac{V_M}{2(t(dY/dx)^R)} \left[ (1 - Y^*) \int_{x^*}^{R} \frac{Y}{V_M} \, dx + Y^* \int_{x^*}^{L} \frac{1-Y}{V_M} \, dx \right] \tag{14}
$$

Where

$$
Y = \frac{N - N^R}{N^L - N^R}
$$

$N$, $N^R$, $N^L$ denote the mole fraction of the component at any position, at the right terminal end of the couple, and at the left terminal end of the couple, respectively.

As indicated $\bar{D}_c$ is composition dependent therefore it is valid only at the specific composition for which it was determined

### 2.2.2 Average Effective Interdiffusion

The average effective interdiffusion coefficient provides a composite value for diffusivity valid over a specified composition range.[15]. For example, for a composition
range, the integral of the flux over an interval from $x_1$ to $x_2$, corresponding to the position at which the composition is $C_1$ and $C_2$, respectively, divided by that composition range gives the average effective interdiffusion coefficient as [16] Equation 15

$$\bar{D}_{eff} = -\frac{\int_{x_1}^{x_2} J dx}{(c_{x_2} - c_{x_1})}$$

The average effective interdiffusion coefficient can be compared more easily to other diffusion coefficients.

2.3 Diffusion Studies in the Mg-Al Binary System

Interdiffusion in the Mg-Al binary system has been studied by a number of researchers. In 2004, Brubakers and Liu[17] presented their study on the phase relations within the Mg-Al binary system when exposed to temperatures between 360°C and 420°C. The formation and growth of $\beta$-$\text{Mg}_2\text{Al}_3$, $\gamma$-$\text{Mg}_{17}\text{Al}_{12}$ and $\epsilon$ phase were characterized. The developed microstructure is shown in Figure 3. The $\beta$ phase grew thickest and had the highest growth constants. The $\epsilon$ phase only formed at the lowest temperatures (<370°C). From data presented, the activation energy was determined for both $\beta$-$\text{Mg}_2\text{Al}_3$, $\gamma$-$\text{Mg}_{17}\text{Al}_{12}$ phases, the activation energy for $\beta$ was lower than that for $\gamma$. Because of the limited data for the $\epsilon$ phase, the activation energy was not calculated. Diffusion coefficients were not reported in Brubake and Liu’s study.
A similar but more comprehensive study was carried out by Brennan,[3] using solid diffusion couples of Mg and Al. She examined the diffusion reactions in the Mg-Al system at temperatures between 250°C and 400°C. The intermetallic phases \(\beta\)-Mg\(_2\)Al\(_3\), \(\gamma\)-Mg\(_{17}\)Al\(_{12}\), formed while the \(\varepsilon\) phase did not. Representative electron micrographs are presented in Figure 4. Like Brubaker and Liu, Brennan noted that the \(\beta\) phase grew thicker and had lower activation energy than the \(\gamma\) phase. The interdiffusion and average effective interdiffusion coefficients were determined with consideration of the variation in molar volume of the intermetallic phases. Brennan reported the relative interdiffusivity to be, from fastest to the slowest, \(\beta\)-Mg\(_2\)Al\(_3\)→\(\gamma\)-Mg\(_{17}\)Al\(_{12}\)→Al→Mg

Most recently, K. Kulkarni and Luo[12] investigated the formation and growth of diffusion reaction products. Similar to work performed by previously mentioned researchers, pure Mg was diffusion bonded to pure Al and subjected to anneal temperatures between 380°C and 420°C. As in Brennan’s study, \(\beta\)-Mg\(_2\)Al\(_3\) and \(\gamma\)-Mg\(_{17}\)Al\(_{12}\) nucleated but \(\varepsilon\) did not form. The \(\gamma\) phase grew slower than \(\beta\) as \(\gamma\) phase activation energy is significantly higher. By varying the isothermal anneal times, Kulkarni and Luo were also able to determine the incubation time for nucleation. The incubation time for \(\beta\) is much larger than that for \(\gamma\). Composition dependent interdiffusion coefficients were calculated however the average effective interdiffusion coefficient was not. The previously identified trends in diffusivity of the phases held true in this study. While in just the last 10 years, the Mg-Al binary system has been repeatedly studied. The effects of alloying Al on the diffusive phase transformations of the
Mg-Al system have not been studied.

Figure 3: Light micrograph of (a) 415°C (b) 367°C diffusion couples

Figure 4: Backscatter electron micrographs from Mg vs. Al diffusion couples annealed at (a) 300°C for 30 days, (b) 350°C for 15 days, and (c) 400°C for 10 days. x_m is the marker plane[18]
CHAPTER 3: EXPERIMENTAL DETAILS

3.1 Materials

In this experiment, we adopted pure Mg (99.99%) and Aluminum Alloy 6061 as the solid-to-solid diffusion materials. With the solid-to-solid diffusion technique, we studied interdiffusion behavior of Mg and AA6061. The pure Mg (Polycrystalline, 99.9%) was commercially procured from SCI Engineered Materials, Inc.™. The components of AA6061 are listed in Table 1.

Table 1: Components of AA6061

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>95.8 - 98.6</td>
</tr>
<tr>
<td>Si</td>
<td>0.4 - 0.8</td>
</tr>
<tr>
<td>Ti</td>
<td>Max 0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>Max 0.25</td>
</tr>
<tr>
<td>Cr</td>
<td>0.04 - 0.35</td>
</tr>
<tr>
<td>Cu</td>
<td>0.15 - 0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>Max 0.7</td>
</tr>
<tr>
<td>Mg</td>
<td>0.8 - 1.2</td>
</tr>
<tr>
<td>Mn</td>
<td>Max 0.15</td>
</tr>
<tr>
<td>Other, each</td>
<td>Max 0.05</td>
</tr>
<tr>
<td>Other, total</td>
<td>Max 0.15</td>
</tr>
</tbody>
</table>

During the experimental process, we sectioned the pure Mg and AA6061 into discs which were 10mm in diameter and 2mm in thickness. To assemble the diffusion couples, the materials were pre-prepared metallographically. Polishing both of the Mg and AA6061
started from 600 grit silicon carbide (SiC) paper; and end up with 1μm alumina suspension. In consideration of the highly reactive chemical properties of pure Mg and Aluminum, the lubricant liquid of each stage of the polishing process was ethanol or oil-based. The contact with water was avoided to minimize the possibility of oxidation.

3.2 Process of Making Diffusion Couples

After delicate polishing of the materials, the Mg and AA6061 discs were assembled with 2mm-thick inert. The diffusion couples were assembled in a stainless steel jig. In order to avoid the contact of materials and stainless steel, each side of the diffusion had an alumina spacer installed. To better illuminate the structure of the diffusion couple, there is a schematic shown in Figure 5.

Figure 5: Schematic of solid-to-solid diffusion couple jig
The diffusion couple jig assemblies were placed in quartz capsules along with a small strip of tantalum foil, intend to absorb oxygen which may evolve during the heating process. The quartz capsule was closed with a small cap which was welded using standard flameworking techniques. After the seal, the capsule was evacuated by flush with hydrogen and high purity argon being pulled to a final vacuum pressure of $\sim 10^{-4}$ Pa ($10^{-6}$ Torr) before final sealing. An encapsulated diffusion couple assembly is shown in Figure 6.

![Figure 6: Encapsulated diffusion couple assembly](image)

### 3.3 Diffusion Anneal

After the preparation of the diffusion couples, each capsule was placed in a preheated Paragon Bluebird™ furnace. External thermocouples were used to monitor and control the temperature.

In this study, three particular temperatures and times were selected based on the phase diagram and related studies. Three diffusion couples were assembled for 573K, 623K and
673K (300°C, 350°C, 400°C) for 720, 360, 240 hours, respectively. The diffusion temperature and relative time is listed in Table 2

<table>
<thead>
<tr>
<th>Couple</th>
<th>Temperature (°C)</th>
<th>Time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg vs.AA6061</td>
<td>300</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>240</td>
</tr>
</tbody>
</table>

After annealing, the quartz capsule was quenched into the cold water at room temperature. The entire diffusion couple jig was cold mounted in the epoxy and, after achieve full cure, sectioned with Buehler IsoMet™ low-speed saw and diamond wafering blade. Then the bonded couple was metallographically polished down to 1 μm. The cutting and polishing process avoided oxidation media as well. Every diffusion couple was checked under OM before doing SEM or TEM to make sure they have good bonding. A SEM (Zeiss Ultra 55 SEM with XEDS) was used to characterize the interdiffusion zone. In scanning electron microscopy, an electron beam is raster across the specimen. The primary electrons interact with the specimen generating secondary electrons (SE), backscattered electrons (BSE), and characteristic x-rays backscatter (BS); Secondary electrons give topographical information about the specimen. 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. The energy of the dispersed characteristic x-rays provide elemental information. The polished couple cross sections were coated with a gold/platinum film to
acidoid charging. By using SEM, the formation of different phases, the microstructure of the whole interdiffusion zone, the thickness of each phase were evaluated. With XEDS, the concentration profiles for each diffusion couple were measured which were further analyzed to reveal the diffusion properties. Additionally, using results of XEDS, get the composition of intermetallic phases.
CHAPTER 4: RESULTS

4.1 Interdiffusion Microstructure and Intermetallic Phase Growth

Backscatter electron micrographs of the three diffusion couples are presented in Figure 7. In the micrograph, there are two obvious intermetallic layers. Characterization with SEM and XEDS and based on Mg-Al diagram shown in Figure 7, the phase near Mg is $\gamma$-Mg$_{12}$Al$_{17}$ and the phase adjacent to AA6061 is $\beta$-Mg$_2$Al$_3$. The $\gamma$ phase is less thick than the $\beta$ phase in each sample, but $\gamma$ has larger solubility range than $\beta$. This result is consistent with other Mg-Al diffusion studies well.[12, 17, 19] In addition to $\beta$ and $\gamma$, a third intermediate phase is reflected in this phase diagram, $\varepsilon(r)$, exists above 250°C, below 410°C. As is shown in Figure 8. However, in many Mg-Al interdiffusion studies, this phase formation has not occurred.[12, 19] In this study, a very thin layer of this phase is observed during the SEM characterization process of couples annealed at both 350°C and 300°C samples. The micrograph is shown in Figure 9. The $\varepsilon$ phase lies between $\gamma$ phase and $\beta$ phase, parallel to these two phases, but is discontinuous, the thickness varies significantly. Elemental analysis with XEDS reveals a composition which is consistent with that of the $\varepsilon$. Since many previous researchers had not identified the presence of $\varepsilon$ phase in Mg-Al diffusion reaction products, additional characterization was performed. A TEM specimen was extracted from the interface between $\gamma$ phase and $\beta$ phase at 350°C using focused ion beam in-situ lift-out. Figure 10 shows the diffraction pattern of $\varepsilon$ phase. This result agrees with other studies in terms of $\varepsilon$ phase.[20, 21]
Figure 7: Backscatter Electron Micrographs of Mg vs. AA6061 diffusion couples at (a) 300°C for 30 days, (b) 350°C for 15 days, and (c) 400°C for 10 days
Figure 8: Mg-Al phase diagram[22]

Figure 9: Micrograph of ε Phase at (a)300°C, (b)350°C
Interdiffusion concentration profiles for each element are obtained from XEDS line scan process. The 350℃ line scan raw data is presented in Figure 11 to represent all the diffusion couples results. As can be seen, the elements besides Al in AA6061 have inconsequential impacts on the reaction products because the concentration of these elements is too low to contribute to have any impact. Only the Mg and Al are relevant and, as such, were normalized and fitted to analyze the diffusion coefficients. Figure 12 shows the fitted concentration profiles for all of the three interdiffusion samples.
Figure 11: Concentration profile raw data of each elements from line scan at 350°C
Figure 12: Fitted Concentration Profiles (a) 300°C for 30 days, (b) 350°C for 15 days, and (c) 400°C for 10 days

ImageJ™ was employed to analyze the backscatter micrograph determine the thickness of each layer. A minimum of 20 random locations were measured for each phase. To calculate
the parabolic growth constant, use Equation 4. The thickness of each layer and the parabolic growth constant are reported in Table 3. Also, the table gives a general comparison of activation energies of this study and previous Mg Vs. pure Al studies,[12, 19] to see the differences between Al and aluminum alloy on diffusion process. Also, this study calculated the growth constant of ε phase. Since this phase was limited to the diffusion couples annealed at 350°C and 300°C, the plot of growth constant doesn’t shown this phase in Figure 13.

Table 3: Thickness, Parabolic growth constants, Pre-exponential factors, Activation energies

<table>
<thead>
<tr>
<th>Y(μm)</th>
<th>γ</th>
<th>β</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>400C/10D</td>
<td>195.57</td>
<td>526.16</td>
<td></td>
</tr>
<tr>
<td>350C/15D</td>
<td>57.93</td>
<td>271.83</td>
<td>9.48</td>
</tr>
<tr>
<td>300C/30D</td>
<td>49.73</td>
<td>320.03</td>
<td>8.05</td>
</tr>
<tr>
<td>K_p(m²/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400C/10D</td>
<td>2.2E-14</td>
<td>1.6E-13</td>
<td></td>
</tr>
<tr>
<td>350C/15D</td>
<td>1.3E-15</td>
<td>2.9E-14</td>
<td>3.5E-17</td>
</tr>
<tr>
<td>300C/30D</td>
<td>4.8E-16</td>
<td>2.0E-14</td>
<td>1.3E-17</td>
</tr>
<tr>
<td>K_0(m²/s)</td>
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<td></td>
<td></td>
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<tr>
<td>4.0E-5</td>
<td></td>
<td></td>
<td>1.0E-8</td>
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<tr>
<td>Q_k(KJ/mol)</td>
<td>120.8</td>
<td>65.4</td>
<td></td>
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</tbody>
</table>
Figure 13: Temperature-dependence of the parabolic growth constants for the $\gamma$-Mg$_{17}$Al$_{12}$ and $\beta$-Mg$_2$Al$_3$ phases determined from layer thickness measurements after diffusion annealing.

4.2 Average Effective Interdiffusion Analysis

Average effective interdiffusion coefficients were determined using Equation 15. The activation energy and pre-exponential factor for interdiffusion in each phase were then calculated using average effective interdiffusion coefficient. Average effective interdiffusion coefficients are reported in Table 4. Figure 14 shows the flux of Mg and Al in different temperature diffusion couples. Figure 15 presents the average effective interdiffusion coefficients for each phase as a function of temperature. The pre-exponential factors and activation energies for interdiffusion coefficients are reported in Table 5. The activation energy for the interdiffusion coefficient in the $\beta$-Mg$_2$Al$_3$ phase is smaller than that of
\( \gamma\)-Mg\(_{17}\)Al\(_{12} \), AA6061 and Mg phases. Also noted is that the smaller activation energy for interdiffusion of AA6061 in Mg than Mg in AA6061.

Figure 14: Flux of Mg and Al in (a) 300 °C for 30 days, (b) 350°C for 15 days, and (c) 400 for 10 days diffusion couples

Table 4: Average effective interdiffusion coefficients

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mg</th>
<th>( \gamma)-Mg(<em>{17})Al(</em>{12} )</th>
<th>( \beta)-Mg(<em>{2})Al(</em>{3} )</th>
<th>AA6061</th>
</tr>
</thead>
<tbody>
<tr>
<td>673K</td>
<td>6.77E-15</td>
<td>1.08E-13</td>
<td>2.13E-12</td>
<td>1.60E-14</td>
</tr>
<tr>
<td>623K</td>
<td>1.80E-15</td>
<td>1.57E-14</td>
<td>5.27E-13</td>
<td>7.36E-15</td>
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<tr>
<td>573K</td>
<td>6.56E-16</td>
<td>6.86E-15</td>
<td>2.16E-13</td>
<td>1.31E-15</td>
</tr>
</tbody>
</table>
Table 5: Activation energies and pre-exponential factors for average effective interdiffusion coefficients

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>γ</th>
<th>β</th>
<th>AA6061</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(KJ/mol)</td>
<td>74</td>
<td>87.2</td>
<td>72.8</td>
<td>80.9</td>
</tr>
<tr>
<td>(D_0)(m(^2)/s)</td>
<td>4.0E-9</td>
<td>5.0E-7</td>
<td>8.0E-7</td>
<td>3.0E-8</td>
</tr>
</tbody>
</table>

Figure 15: Activation energies and pre-exponential factors for average effective interdiffusion coefficients
CHAPTER 5: DISCUSSION

5.1 Interdiffusion Analysis Methodology

When changes in molar volume occur across the interdiffusion zone, the method analysis of coefficients may require modification. If the molar volume deviates significantly from Vegard’s linear relationship, the Boltzmann-Matano method will yield erroneous results. In such cases, a correction factor can be applied, as done by Brennan [12], or an alternative method, such as the Sauer-Freise method, must be implemented. In this study, the Boltzmann-Matano method was used without correction. To demonstrate that the deviation from Vegard’s rule is insignificant, interdiffusion coefficients were calculated for the couple annealed at 400°C for 10 days using both the Boltzmann-Matano method and the Sauer-Freise method. The interdiffusion coefficients were plotted as a function of Mg concentration and are presented in Figure 16. The greatest deviation occurs in the γ phase where the molar volume is 12.2 cm³/mol – Vegard’s rule would suggest the molar volume 11.7 cm³/mol – and represents a deviation of almost 5%. As can be seen, the Sauer-Freise method gives virtually identical results as the Boltzmann-Matano method. This suggests that the deviation from Vegard’s rule is inconsequential and changes in molar volume across the diffusion zone in the Mg-AA6061 system can be neglected.
Figure 16: Interdiffusion Coefficients of 400°C diffusion couples use Sauer-Freise Method and Boltzmann-Matano Method

5.2 Microstructural Features of Intermetallic Phases

Based on the phase diagram, there are three possible intermetallic phases in the Mg-Al system between 300°C and 400°C. Previous studies have reached an agreement in terms of the existence of γ phase and β phase and their solubility range. However, the existence of ε phase has been inconsistently reported. Lots of studies were done trying to find this phase. The ε phase was first examined by Murray. [23] As assessed by Murray, there is a stoichiometric phase known as ε(r) with a composition of 42 at.% Mg, that exists between 320°C and 370°C. The other assessments of this phase and their phase diagrams are shown in Figure 17.[21, 24, 25] Based on these phase diagrams the ε phase exits in differing
temperature ranges and solubility limits. In Zuo and Liang’s works, ε phase is an intermetallic line compound, however in Su’s phase diagram, ε has some solubility range. In a study of the Mg-Al system within the temperature range of $360^\circ \text{C}$ to $420^\circ \text{C}$, Brubaker and Liu [17] reported the formation of a thin layer of the ε-phase in diffusion couples annealed at $367^\circ \text{C}$ and $360^\circ \text{C}$. In contrast, an earlier investigation of the system in the temperature range of $325^\circ \text{C}$ to $425^\circ \text{C}$ by Funamizu and Watanabe [19] reported that the ε-phase did not develop in any of their diffusion couples. In the study by Tanguet Njiokep et al.,[26] it was stated that some diffusion couples developed a very thin layer of the ε-phase observed by optical microscopy but was not verified. Brennan [12] reported the absence of the ε phase and gave a reason that may be explained from a framework that considers solubility range, diffusion coefficients, and thermodynamics [27-30]. The ε-phase has a narrow range of solubility (1.3 at. %) [17] [22], and may be thermodynamically and kinetically unfavorable to nucleate and/or grow relative to the β- and γ-phases. The melting temperature of the ε-phase is lower than its surrounding.

In this study, a narrow layer of ε phase is observed in $300^\circ \text{C}$ and $350^\circ \text{C}$ samples. The thickness measured is less than 10μm, and resides just between γ phase and β phase. Because of the similarity in atomic number between, the contrast under backscatter detector is relatively low and difficult to observe the existence of this phase. Nonetheless, with close examination, this phase was identified. Explained by previous studies, this phase is thermodynamically and kinetically unfavorable, the growth of the other two phases may also
impede the formation of $\varepsilon$ phase. However, the $\varepsilon$ phase may present in the Mg-AA6061 system due to effects of other elements such as Si in AA6061. The presence of alloying elements such as Si, Fe, and Mg in the AA6061 may play an important role in the nucleation of the $\varepsilon$ phase.

An additional observation that can be made from the microstructure of the diffusion zone is that the $\gamma$ phase is much thinner than $\beta$ phase, shown previously in Figure 7. However, the phase diagram shows the solubility of the $\gamma$ phase to be more extensive than that for the $\beta$ phase. As noted, the parabolic growth constant is higher and the activation energy for growth is lower for the $\beta$ phase than the $\gamma$ phase. On the other hand, from Table 4 and Table 5, diffusion occurs faster and more readily in the $\beta$ phase than in the $\gamma$ phase. The balance between the diffusion and growth account for the apparent inconsistency of the diffusion-zone layer thickness.
Intermetallic Phases Growth

The parabolic growth constants were determined from the thickness measurements previously described. Table 6 and Figure 18 present the growth constants of this study alongside results determined in other studies of the binary Mg-Al system. From Table 6 it can be seen that at 400°C and 350°C, the growth constants are lower in this study than determined by Brennan. However, at 300°C the opposite is true; the growth constant is lower in Brennan’s pure binary system than in this study. This implies that the activation energy
differs. Figure 18 shows the Arrhenius relationship for the growth constants of this study as well as data from several different pure Mg-Al studies. The activation energy for growth of \( \gamma \) and \( \beta \) intermetallic phases is lower for the Mg-AA6061 system than for the Mg-Al system.

The activation energy for growth for the \( \beta \) phase is markedly lower than that for the \( \gamma \) phase. Table 7 presents the growth activation energy found in this study and the activation energy reported in several Mg-Al studies. The activation energy of this study for each phase is somewhat lower than that for the pure Mg and pure Al system. This difference can be attributed to the presence of alloying elements in AA6061.

Table 6: Parabolic Growth Constant Comparison

<table>
<thead>
<tr>
<th></th>
<th>( \gamma )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K(_p)(m(^2)/s)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>400C/10D</td>
<td>2.2E-14</td>
</tr>
<tr>
<td></td>
<td>350C/15D</td>
<td>1.3E-15</td>
</tr>
<tr>
<td></td>
<td>300C/30D</td>
<td>4.8E-16</td>
</tr>
<tr>
<td><strong>K(_p)(m(^2)/s)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>by Brennan[12]</td>
<td>400C/10D</td>
<td>2.9E-14</td>
</tr>
<tr>
<td></td>
<td>350C/15D</td>
<td>2.3E-15</td>
</tr>
<tr>
<td></td>
<td>300C/30D</td>
<td>1.7E-16</td>
</tr>
</tbody>
</table>
Figure 18: Comparison of parabolic growth constant of this study and Mg-Al system studies
Table 7: Activation Energy of Growth of $\beta$ phase and $\gamma$ phase in different studies

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>187.7±1.9</td>
<td>185.9</td>
<td>165.0</td>
<td>120.8</td>
</tr>
<tr>
<td>$\beta$</td>
<td>37.3±4.1</td>
<td>83.2</td>
<td>85.5</td>
<td>65.4</td>
</tr>
</tbody>
</table>
CHAPTER 6: SUMMARY & CONCLUSIONS

In this study, the interdiffusion behavior of Mg-AA6061 system was investigated. The solid-to-solid state diffusion couple is the basis of this experiment. A total of three diffusion couples were assembled. The annealing temperatures for the three diffusion couples are 300°C, 350°C, and 400°C. Previous studies focused on the Mg-Al system at this temperature range while the interdiffusion behavior between Mg and alloyed Al has not been previously examined. For purposes of comparison of this study with Mg-Al studies common diffusion anneal temperatures have been chosen. After careful preparation and fine polishing, diffusion couples were characterized with optical microscopy, electron microscopy, and energy dispersive spectroscopy. To yield results presented herein.

The presence of the ε phase in the 300°C and 350°C diffusion couples were confirmed by using electron microscopy equipped with a backscatter electron detector. By closely and carefully checking the interfacial plane of γ phase and β phase, a subtle layer of contrast difference was observed, indicative of an additional phase. The thickness of the layer is small, less than 10μm, and the continuity of this layer is not well maintained. Compositional analysis via XEDS implicated the presence of a separate phase consisted with the ε phase. [1] In order to get more definitive evidence to confirm the presence of this phase, TEM and electron diffraction were performed.
TEM results gave a sound support towards the existence of $\epsilon$ phase. Evident from the Mg-Al phase diagram, the solubility range of the $\epsilon$ phase is very small. This phase is relatively thermodynamically unfavorable compared with the other two Mg-Al intermetallics, which may be a main reason this phase is absent in many studies. Alloying elements other than Mg exist in the AA6061 alloy. These elements may affect the diffusion reaction, especially the formation of intermetallic phases. One clear conclusion is that the alloying elements do not affect the growth of the $\gamma$ and $\beta$ phases. This conclusion is founded in the comparison between growth constants determined in the Mg-Al binary phase with those from this study of Mg-6061. The growth activation energy of $\beta$ phase is lower than that of $\gamma$ phase. Even though $\gamma$ phase has larger solubility range in the phase diagram, $\beta$ phase is thicker than $\gamma$ phase.

This study adopted different methods to calculate the interdiffusion coefficients. The diffusion couple annealed at 400°C was used as a comparative basis for analysis methods. Interdiffusion coefficients were calculated based on the Boltzmann-Matano method and the Sauer-Freise method. In addition, the results were compared with results from Mg-Al couples annealed under similar parameters. It was confirmed that there is insignificant molar volume change in the interdiffusion zone of this study hence the Boltzmann-Matano method is valid to calculate the interdiffusion coefficients for each phase.
REFERENCES


