Diffusion in the Mg-Al system

Sarah Brennan¹, Katrina Bermudez¹, Nagraj Kulkarni², Yongho Sohn²
¹University of Central Florida, Advanced Materials Processing and Analysis Center
Department of Mechanical, Materials and Aerospace Engineering, Orlando, FL, 32816, USA
²Oak Ridge National Laboratory, Measurement Science & Systems Engineering Division
Oak Ridge, TN, 37831, USA
Magnesium (Mg) based alloys are among the lightest weight materials available for use in military, electronics and transportation applications.

Fundamental knowledge of high-fidelity diffusion properties in Mg alloys can enhance development and optimization for design, processing, manufacturing and applications of new and existing alloys.

Despite the great potential for many applications, diffusion properties for Mg and Mg-alloys are scarce, and predate the recent interest.

Al is the most common alloying element in commercial Mg-alloys. Furthermore, Mg is one of the common alloying elements in commercial Al-alloys. Previous works on Mg-Al interdiffusion [*] has raised some discrepancy in microstructural features and the composition-dependence of interdiffusion coefficients were not fully reported.

In this study, interdiffusion using the solid-to-solid diffusion couple technique was employed to investigate the binary Mg-Al system.

Solid-to-solid diffusion couples were assembled and annealed at 300°C, 350°C and 400°C for 720, 360, and 240 hours, respectively.

Microstructural development was examined by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with X-ray energy dispersive spectroscopy (XEDS).

Concentration profiles for each diffusion couple were acquired using electron microprobe analysis (EPMA).

The thicknesses of each phase were measured and used to determine parabolic growth constants and activation energies.

Composition-dependent interdiffusion coefficients in Mg- and Al-solid solutions, \( \gamma\)-\( \text{Al}_{12}\text{Mg}_{17} \) and \( \beta\)-\( \text{Al}_{3}\text{Mg}_{2} \) phases were calculated based on Boltzmann-Matano analysis.

An identifiable Kirkendall marker plane located in the \( \beta\)-\( \text{Al}_{3}\text{Mg}_{2} \) phase near the Al side of the diffusion microstructure was utilized, in conjunction with the concentration profile, to determine the intrinsic diffusion coefficients of Mg and Al in the \( \beta\)-\( \text{Al}_{3}\text{Mg}_{2} \) phase.

Activation energies and the pre-exponential factors for the inter- and intrinsic diffusion coefficients were also calculated.
Thickeness of the intermetallic layers that formed in the reaction zone were measured using image analysis and the growth constants, \( k_p \), found assuming a parabolic relation:

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

where \( Y \) is the layer thickness and \( t \) is the annealing time.

Activation energies, \( Q_k \), for growth of each intermetallic phase were determined from the Arrhenius relation:

\[
k_p = k_o \exp \left[ \frac{-Q_k}{RT} \right]
\]

Where \( R \) is the ideal gas constant and \( T \) is the absolute annealing temperature.
Each phase was curved fitted using polynomial function, up to the 3\textsuperscript{rd} order.

The variation in the molar volume was accounted for by dividing the molar volume of the phase from the phase’s concentration profile and assuming the molar volume remained constant within a given phase.

Boltzmann-Matano was used to determine the interdiffusion flux, first finding the Matano plane [1-2]

$$\int_{C_i^+}^{C_i^0} x dC_i + \int_{C_i^0}^{C_i^{-\infty}} x dC_i = 0$$

where $C_i^{+\infty}$ refers to the terminal ends of the diffusion couple and $C_i^D$ refers to the Matano plane.

With the Matano plane, the interdiffusion flux ($J_i$) for each phase was calculated using [3]

$$J_i = \frac{1}{2t} \int_{C_i^0}^{C_i^{+\infty}} (x - x_o) dC_i$$

where $x_o$ is the location of the Matano plane.

The interdiffusion coefficient ($\bar{D}_i$) was calculated by combining Fick’s law with the two equations

$$\bar{D}_i = \frac{1}{2t} \int_{C_i^0}^{C_i^{+\infty}} (x - x_o) dC_i$$

\[\frac{\partial C_i}{\partial x}\]

Concentration profiles were curve fitted using polynomial functions up to the 3rd order.

Intrinsic diffusion coefficients were determined using Heumann’s Method* which uses the accumulated intrinsic flux at the marker plane

The accumulated intrinsic flux ($A_i$) is defined by

$$ A_i = \int_0^t J_i = -\int_0^t D_i \frac{\partial C_i}{\partial x_m} dt $$

The expression is rearranged to solve for the intrinsic diffusion coefficient

$$ D_i = - \frac{A_i}{2t \left[ \frac{\partial C_i}{\partial x} \right]_{x_m}} $$

Mg-Al diffusion couples were encapsulated in quartz capsules.
Flushed three times and backfilled with high purity Ar to 1 atm at the annealing temperature.
Water quenched after anneal and mounted in epoxy before cross-sectioned.
Metallographically polished from 600 grit to 1 μm alumina.
OM for bond quality check.
SEM for phase constituents.
EPMA for raw data line scans.

Temperature (°C) | Time
--- | ---
300 | 30 days
350 | 15 days
400 | 10 days
Results: Diffusion microstructure and concentration profile

300°C 30 days

(a)
Results: Diffusion microstructure and concentration profile

350°C 15 days
Results: Diffusion microstructure and concentration profile

$400^\circ C$ 10 days

(c)
Results: Growth constants and activation energy

Arrhenius plot of growth constants for the intermetallic phases

- The activation energy for the γ-phase is significantly higher than that of the β-phase
- This trend was also reported by Funamizu and Watanabe*

<table>
<thead>
<tr>
<th>Y [std. dev] (μm)</th>
<th>Phase</th>
<th>400°C/10 days</th>
<th>350°C/15 days</th>
<th>300°C/30 days</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>k_p (m^3/s)</th>
<th>Phase</th>
<th>400°C/10 days</th>
<th>350°C/15 days</th>
<th>300°C/30 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al_{12}Mg_{17}</td>
<td>2.9x10^{-14}</td>
<td>2.3x10^{-15}</td>
<td>1.7x10^{-16}</td>
<td></td>
</tr>
<tr>
<td>β-Al_{3}Mg_{2}</td>
<td>2.1x10^{-13}</td>
<td>8.9x10^{-14}</td>
<td>1.4x10^{-14}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Q_k (kJ/mol)</th>
<th>Phase</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al_{12}Mg_{17}</td>
<td>165.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Al_{3}Mg_{2}</td>
<td>85.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Q_k (kJ/mol) [+]</th>
<th>Phase</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al_{12}Mg_{17}</td>
<td>143.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Al_{3}Mg_{2}</td>
<td>62.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results: Interdiffusion

Interdiffusion as a function of concentration

- Interdiffusion in the β-phase remains constant within its composition range
- Within the γ-phase, interdiffusion decreases with increasing Mg concentration
- Interdiffusion within both terminal solid solutions is seen to decrease as the concentration of the respective solute decreases.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mg s.s.</th>
<th>γ-Al₁₂Mg₁₇</th>
<th>β-Al₃Mg₂</th>
<th>Al s.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>9.3x10⁻¹⁵</td>
<td>1.4x10⁻¹³</td>
<td>2.5x10⁻¹²</td>
<td>1.9x10⁻¹⁴</td>
</tr>
<tr>
<td>350°C</td>
<td>8.8x10⁻¹⁶</td>
<td>2.3x10⁻¹⁴</td>
<td>7.3x10⁻¹³</td>
<td>2.2x10⁻¹⁵</td>
</tr>
<tr>
<td>300°C</td>
<td>1.9x10⁻¹⁶</td>
<td>2.9x10⁻¹⁵</td>
<td>1.7x10⁻¹³</td>
<td>2.5x10⁻¹⁶</td>
</tr>
</tbody>
</table>

Numerically averaged interdiffusion coefficients for Mg (ss), γ-Al₁₂Mg₁₇, β-Al₃Mg₂, Al (ss) phases.
Results: Interdiffusion

 Activation energies and pre-exponential factors for averaged interdiffusion coefficients for Mg (ss), γ-Al\textsubscript{12}Mg\textsubscript{17}, β-Al\textsubscript{3}Mg\textsubscript{2}, Al (ss) phases.

<table>
<thead>
<tr>
<th></th>
<th>Mg s.s.</th>
<th>γ-Al\textsubscript{12}Mg\textsubscript{17}</th>
<th>β-Al\textsubscript{3}Mg\textsubscript{2}</th>
<th>Al s.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q (kJ/mol)</td>
<td>123.1</td>
<td>124.0</td>
<td>85.6</td>
<td>138.8</td>
</tr>
<tr>
<td>(D_0) (m\textsuperscript{2}/s)</td>
<td>2.7x10\textsuperscript{-5}</td>
<td>5.8x10\textsuperscript{-4}</td>
<td>1.1x10\textsuperscript{-5}</td>
<td>1.1x10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

- The activation energy for the β-phase was determined to be the lowest, while the Al solid solution had the highest.
- The activation energies for the Mg solid solution and the γ-phase are similar, however, the diffusion coefficients are higher for the γ-phase.
Results: Intrinsic diffusion

Intrinsic Diffusion Coefficients for Mg and Al in the $\beta$-$\text{Al}_3\text{Mg}_2$ phase.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Composition (at.% Mg)</th>
<th>Concentration Gradient $[\partial C_{\text{Mg}}/\partial x]_{sw}$</th>
<th>Intrinsic Diffusion Coefficients, $D_i$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>38.2</td>
<td>$7.9 \times 10^7$</td>
<td>$1.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>350°C</td>
<td>37.5</td>
<td>$1.1 \times 10^8$</td>
<td>$3.9 \times 10^{-15}$</td>
</tr>
<tr>
<td>300°C</td>
<td>38.0</td>
<td>$2.6 \times 10^8$</td>
<td>$8.4 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

Activation energy and pre-exponential factor for intrinsic diffusion coefficients of Mg and Al in the $\beta$-$\text{Al}_3\text{Mg}_2$ phase (avg. composition 38 at.% Mg).

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{Mg}}$</th>
<th>$D_{\text{Al}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$ (kJ/mol)</td>
<td>100.0</td>
<td>111.9</td>
</tr>
<tr>
<td>$D_o$ (m$^2$/s)</td>
<td>$1.0 \times 10^{-6}$</td>
<td>$1.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
**Discussion: Extrapolations to impurity diffusion coefficients**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$D_{Al}^{Mg}$ (m$^2$/s)</th>
<th>$D_{Mg}^{Al}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>4.5x10^{-15}</td>
<td>9.4x10^{-15}</td>
</tr>
<tr>
<td>350°C</td>
<td>1.3x10^{-15}</td>
<td>1.2x10^{-15}</td>
</tr>
<tr>
<td>300°C</td>
<td>1.9x10^{-16}</td>
<td>7.6x10^{-17}</td>
</tr>
<tr>
<td>$D_0$ (m$^2$/s)</td>
<td>3.8x10^{-7}</td>
<td>1.0x10^{-2}</td>
</tr>
<tr>
<td>Q (kJ/mol)</td>
<td>101.4</td>
<td>154.6</td>
</tr>
</tbody>
</table>

- Extrapolations of the interdiffusion data made to impurity diffusion of Al in Mg and Mg in Al.
- Literature values of self diffusion and impurity diffusion data plotted for comparison.

In the diffusion microstructures examined in this study, the ε-phase, located between the β-phase and γ-phase, did not develop in any of the diffusion couples. A diffusion study of the Mg-Al system by Brubaker and Liu [1] in the temperature range of 360° to 420°C reported the existence of the ε-phase in diffusion couples annealed at 367° and 360°C. In contrast, an earlier investigation of the system in the temperature range of 325° to 425°C by Funamizu and Watanabe [2] reported that the ε-phase did not develop.

The absence of the ε-phase may be explained from a framework that considers solubility range, diffusion coefficients, and thermodynamics [3-6]. The ε-phase has a narrow range of solubility (1.3 at. %), is thermodynamically unfavorable relative to the β- and γ-phases, and potentially has a lower diffusion coefficient than its surrounding intermetallic phases.

Activation energy for growth and diffusion for the β-phase are 85.5 and 85.6 kJ/mol, respectively. These are essentially the same, suggesting the growth of the β-phase is diffusion controlled.

The parabolic growth activation energy for the γ-phase is 165.0 kJ/mol while its activation energy for diffusion is 124.0 kJ/mol. The difference in these values suggests the growth of the γ-phase is reaction controlled.
Discussion: Microstructural features and Marker Plane Movements

- As shown in the micrographs of the developed interaction layers, a clear marker plane, $x_m$, is identified within the $\beta$-phase near the $\beta$/Al (ss) interface, suggesting Al is the faster moving constituent within the $\beta$-$\text{Al}_3\text{Mg}_2$ phase.
- Porosity is present in the Mg (ss) side of the diffusion microstructure, in particular in the 400°C couple. These pores could suggest that Mg atoms diffuse faster out of the Mg (ss) into the $\gamma$-phase then Al atoms can diffuse across this interface into the Mg (ss), leaving a supersaturation of vacancies in the Mg (ss) leading to porosity.
- A significant amount of oxygen was detected at the $\gamma$/Mg (ss) interface, possibly suggesting a second marker plane [*], however, its position at the interface and close to the pores makes this difficult to confirm.

Ongoing Work

- Diffusion studies of the binary systems:
  - Mg-Zn
  - Mg-Y
  - Mg-Nd
  - Self- and impurity diffusion of stable isotopes $^{25}\text{Mg}$ and $^{68}\text{Zn}$ in single and polycrystalline and single crystal Mg via SIMS depth profiling.
Acknowledgements

- U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, as part of the Lightweight Materials Program
- The Materials Characterization Facility at the University of Central Florida
- Ms. Brennan would like to thank the College of Graduate Studies for the Graduate Travel Award