Diffusion in the Mg-Al system

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Motivation

- 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.

*Y. Funamizu and K. Watanabe, *Trans. Jpn. Inst. Met.*, (1972), Vol. 13, pp.278-83.
* T. Heumann and A. Kottman, *Z. Metallkd.*, (1953), Vol. 44, pp. 139.

Introduction

- 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, γ-$Al_{12}Mg_{17}$ and β-Al_3Mg_2 phases were calculated based on Boltzmann-Matano analysis .
- An identifiable Kirkendall marker plane located in the β-Al_3Mg_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 β-Al_3Mg_2 phase.
- Activation energies and the pre-exponential factors for the inter- and intrinsic diffusion coefficients were also calculated.

Analytical Framework: Growth

- Thicknesses 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.

Analytical Framework: Interdiffusion

- Each phase was curved fitted using polynomial function, up to the 3rd 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]

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

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

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

$$\tilde{J}_i = \frac{1}{2t}\int_{C_i^{\pm\infty}}^{C_i} (x - x_o) dC_i$$

where x_o is the location of the Matano plane

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

$$\widetilde{D}_i = \frac{\frac{1}{2t}\int_{C_i^{\pm\infty}}^{C_i} (x - x_o) dC_i}{\frac{\partial C_i}{\partial x}}$$

[1] L. Boltzmann, *Wein. Ann.*, (1894), Vol. 53, pp. 959.
[2] C. Matano, *Jpn. J. Phys.*, (1933), Vol. 8, pp. 109.
[3] M.A. Dayananda and C. W. Kim, *Metall. Mater. Trans. A*, (1979), Vol. 10A, pp. 1333-39.

Analytical Framework: Intrinsic Diffusion

- 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

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

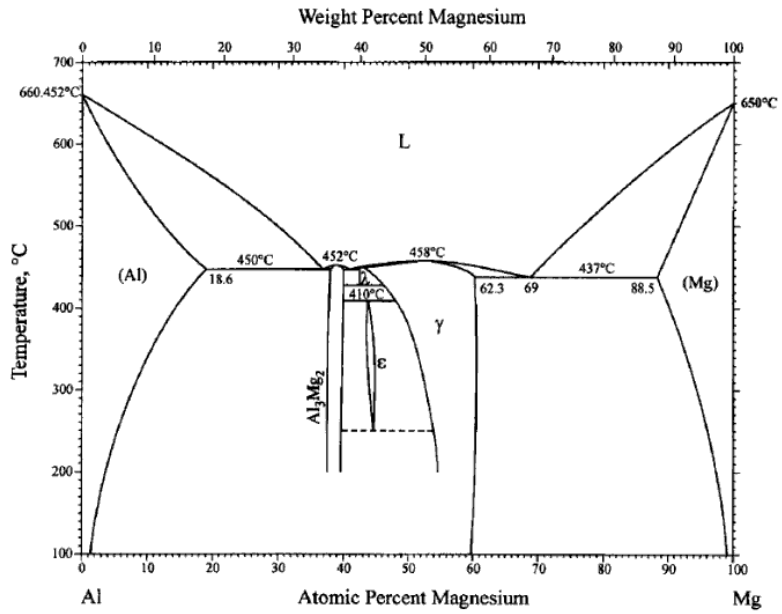
- The expression is rearranged to solve for the intrinsic diffusion coefficient

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

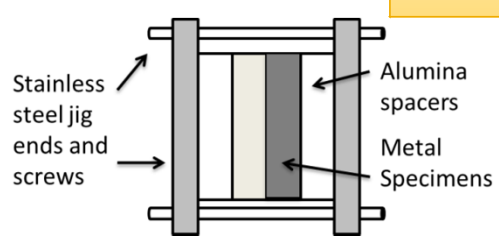
*T. Heumann, *Z. Phys. Chem.*, (1952), Vol. 201, p.168.

Experimental Procedure

- 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

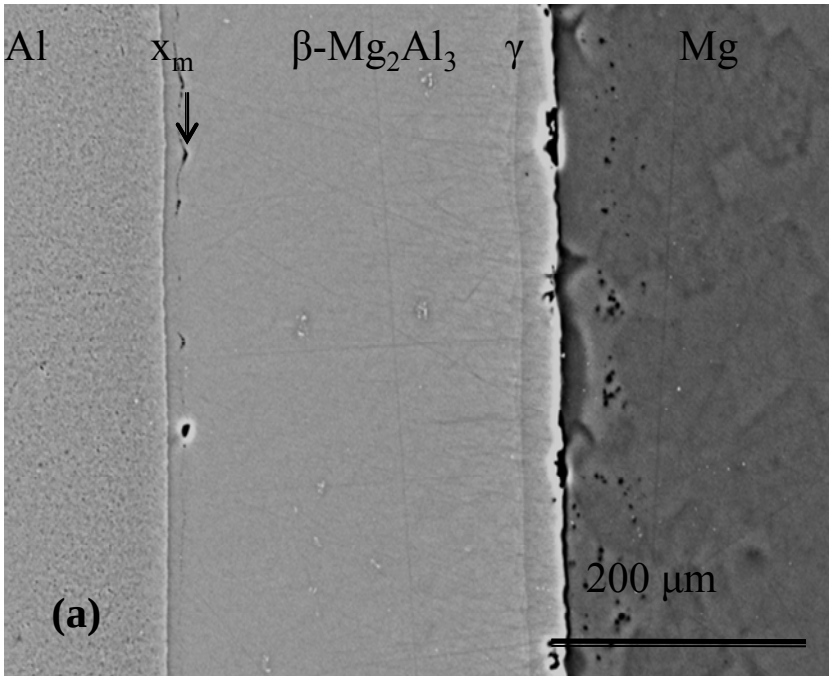


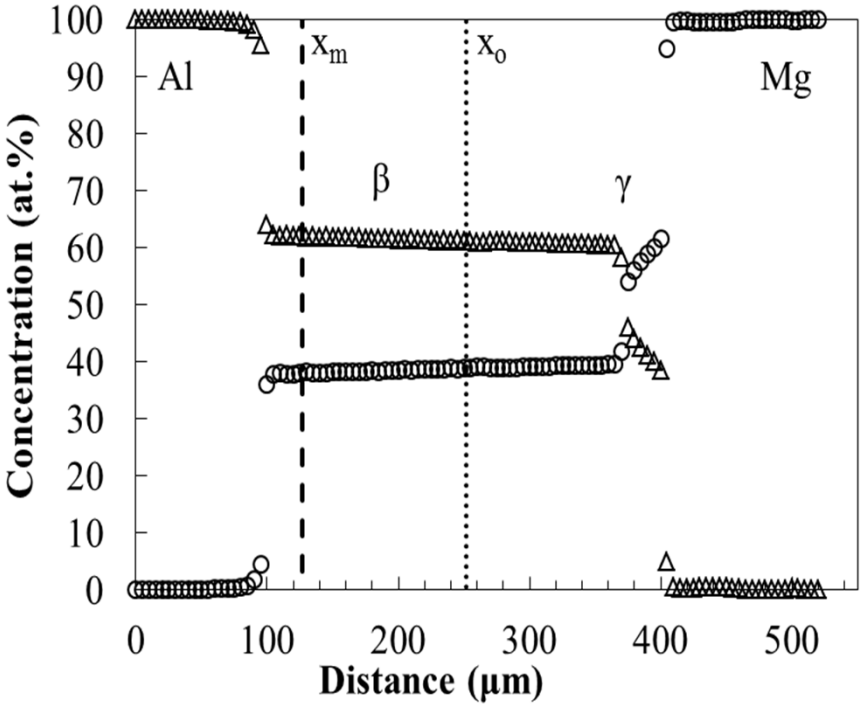
Temperature (°C)	Time
300	30 days
350	15 days
400	10 days



Results: Diffusion microstructure and concentration profile

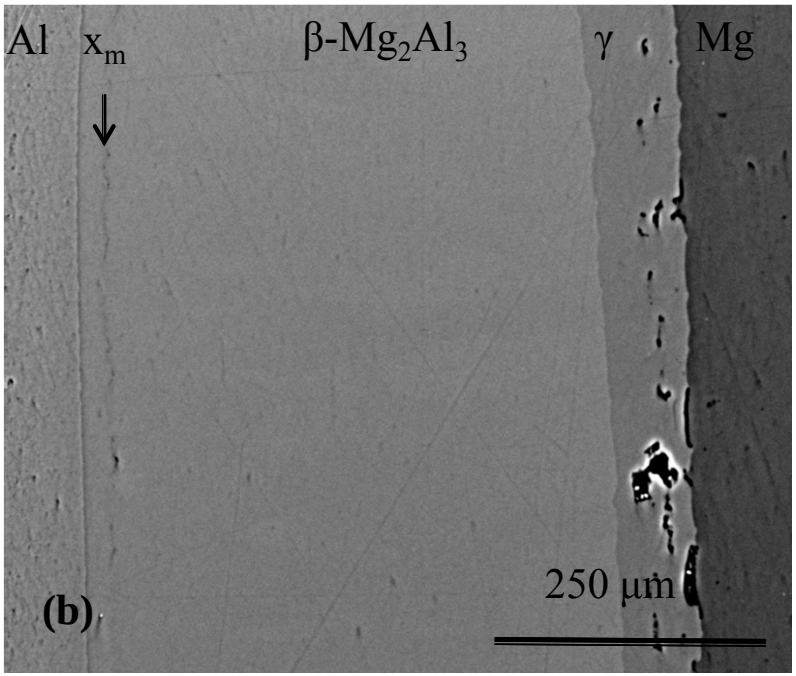
300°C 30 days

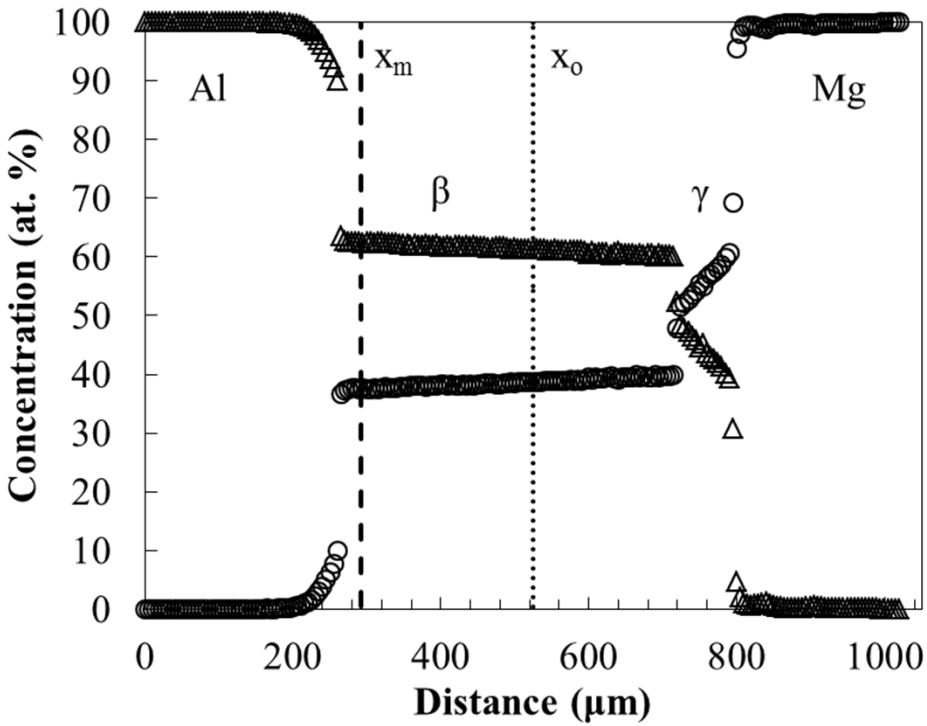




Results: Diffusion microstructure and concentration profile

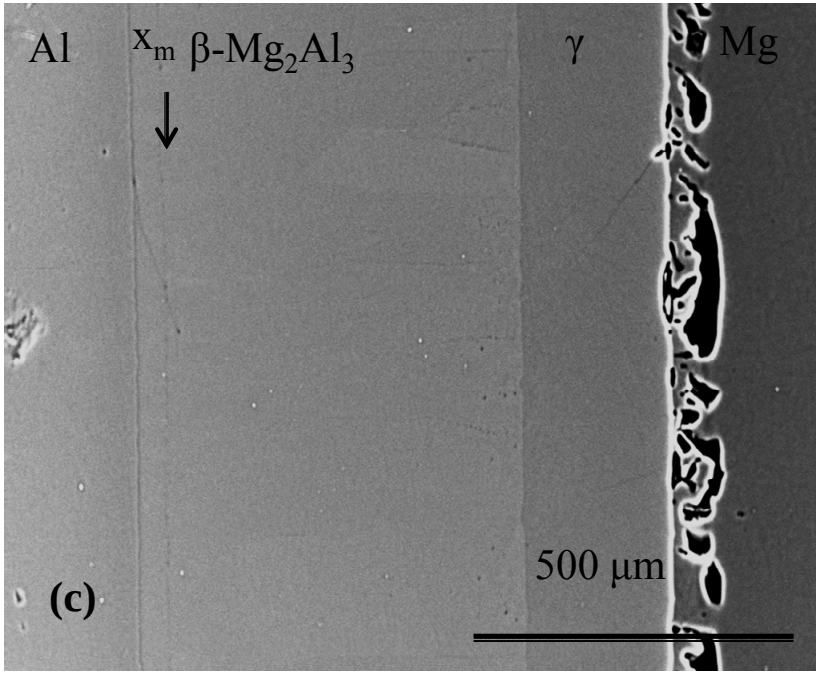
350C 15 days

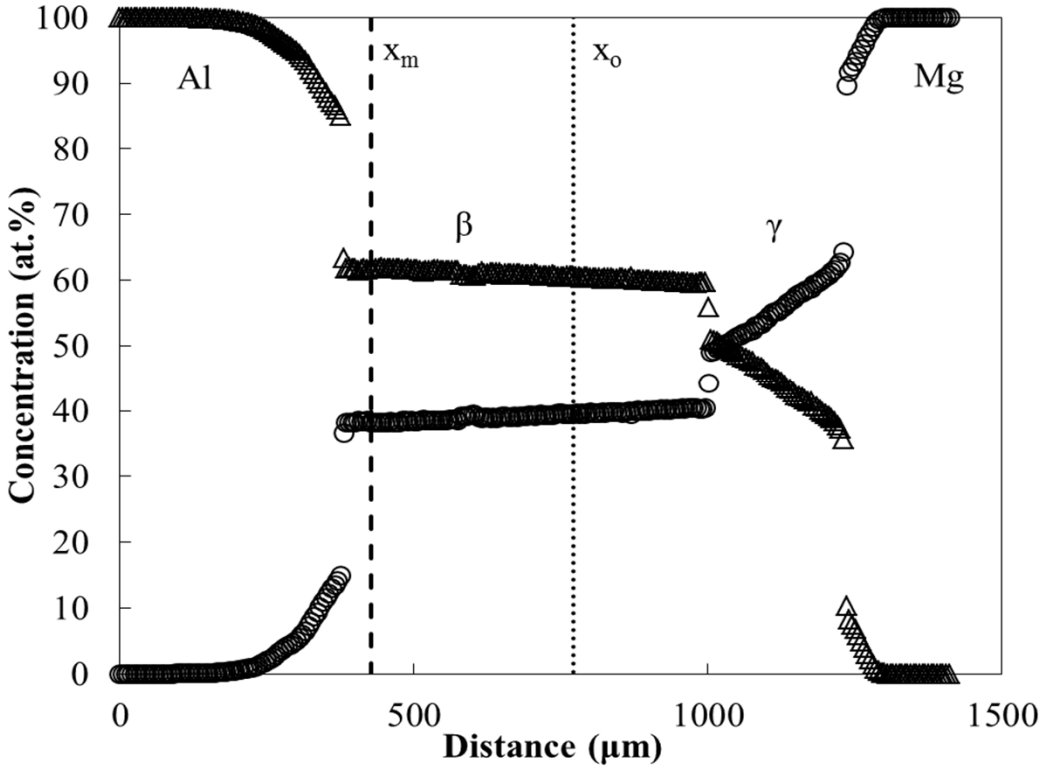




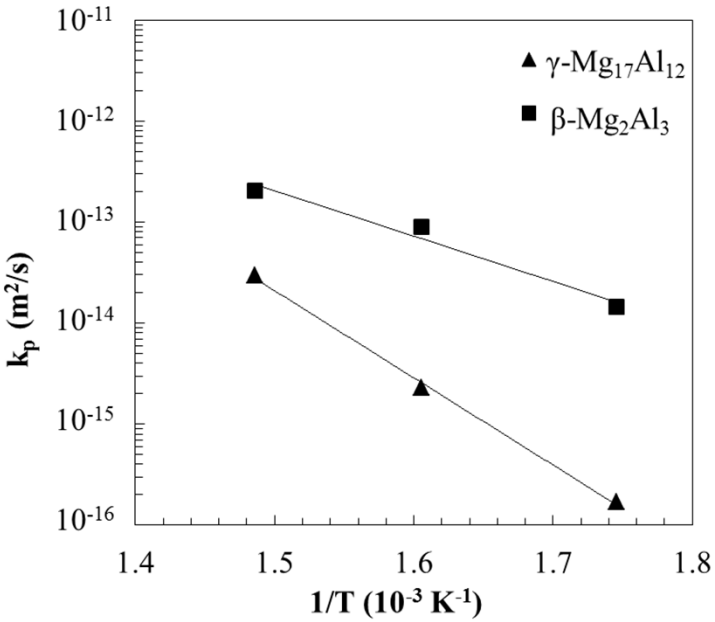
Results: Diffusion microstructure and concentration profile

400C 10 days





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*

Thickness measured from SEM and EPMA comparison, growth constants, pre-exponential factors and activation energies for growth.

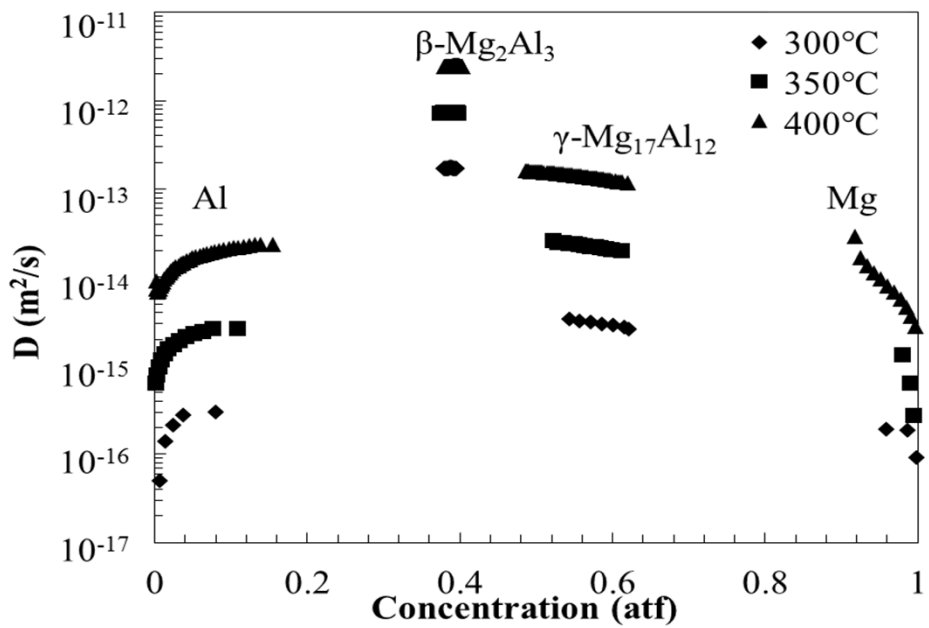
	Phase	400°C/10 days	350°C/15 days	300°C/30 days
Y [std. dev] (μm)	γ-$Al_{12}Mg_{17}$	226 [2]	77 [6]	29 [2]
	β-Al_3Mg_2	595 [3]	481 [5]	273 [2]
k_p	γ-$Al_{12}Mg_{17}$	2.9×10^{-14}	2.3×10^{-15}	1.7×10^{-16}
	β-Al_3Mg_2	2.1×10^{-13}	8.9×10^{-14}	1.4×10^{-14}
Q_k (kJ/mol)	γ-$Al_{12}Mg_{17}$		165.0	
	β-Al_3Mg_2		85.5	
Q_k (kJ/mol) [*]	γ-$Al_{12}Mg_{17}$		143.1	
	β-Al_3Mg_2		62.3	

*Y. Funamizu and K. Watanabe, *Trans. Jpn. Inst. Met.*, (1972), Vol. 13, pp.278-83,

Results: Interdiffusion

Interdiffusion as a function of concentration

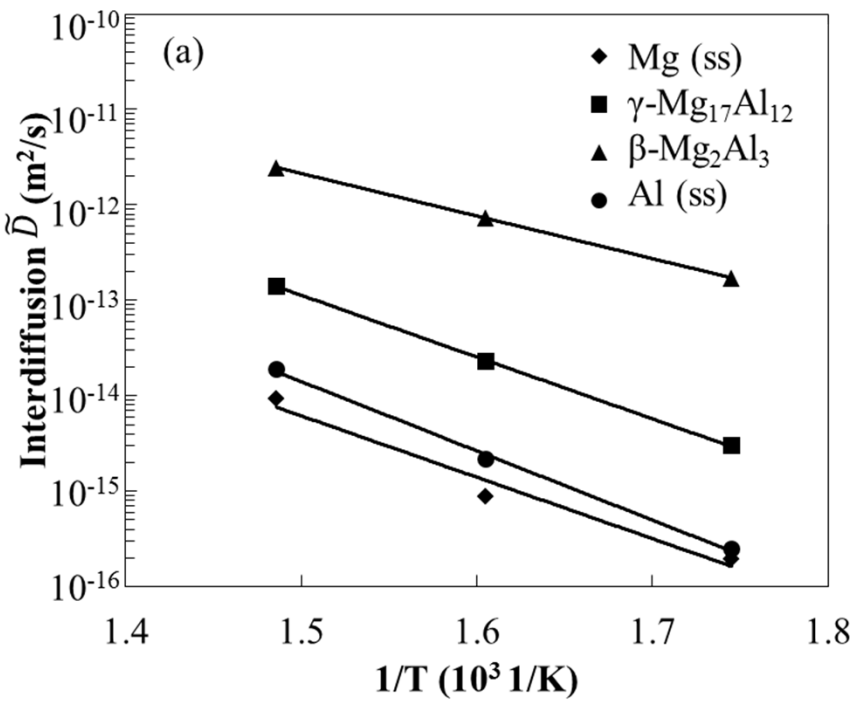
- Interdiffusion in the β-phase remains constant within its composition range
- Within the γ-phase, interdiffusion decreases with increasing Mg concentration
- Interdiffusion within both terminal solid solutions is seen to decrease as the concentration of the respective solute decreases.



	Interdiffusion Coefficients, $\widetilde{D}$ (m²/s)			
Temperature	Mg s.s.	γ-$Al_{12}Mg_{17}$	β-Al_3Mg_2	Al s.s.
400°C	9.3×10^{-15}	1.4×10^{-13}	2.5×10^{-12}	1.9×10^{-14}
350°C	8.8×10^{-16}	2.3×10^{-14}	7.3×10^{-13}	2.2×10^{-15}
300°C	1.9×10^{-16}	2.9×10^{-15}	1.7×10^{-13}	2.5×10^{-16}

Numerically averaged interdiffusion coefficients for Mg (ss), γ-$Al_{12}Mg_{17}$, β-Al_3Mg_2, Al (ss) phases.

Results: Interdiffusion



Temperature dependence of interdiffusion for each phase

Activation energies and pre-exponential factors for averaged interdiffusion coefficients for Mg (ss), γ-$Al_{12}Mg_{17}$, β-Al_3Mg_2, Al (ss) phases.

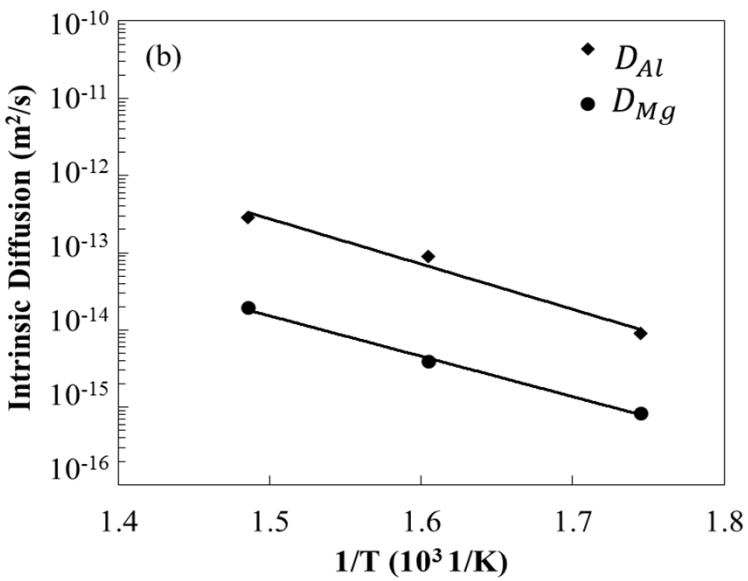
	Mg s.s.	γ-$Al_{12}Mg_{17}$	β-Al_3Mg_2	Al s.s.
Q (kJ/mol)	123.1	124.0	85.6	138.8
D_0 (m^2/s)	2.7×10^{-5}	5.8×10^{-4}	1.1×10^{-5}	1.1×10^{-3}

- 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 β-Al_3Mg_2 phase.

Temperature	Composition (at.% Mg)	Concentration Gradient $\left[\partial C_{Mg}/\partial x\right]_{x_m}$	Intrinsic Diffusion Coefficients, D_i (m^2/s)	
			D_{Mg}	D_{Al}
400°C	38.2	7.9×10^{7}	1.9×10^{-14}	2.9×10^{-13}
350°C	37.5	1.1×10^{8}	3.9×10^{-15}	8.8×10^{-14}
300°C	38.0	2.6×10^{8}	8.4×10^{-16}	8.9×10^{-15}



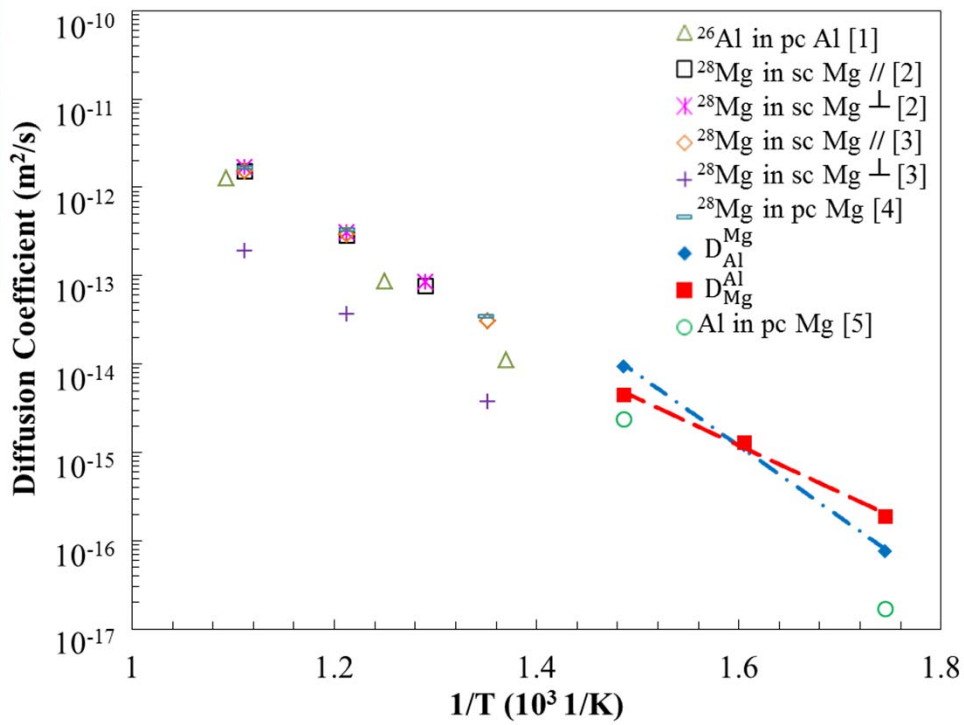
Activation energy and pre-exponential factor for intrinsic diffusion coefficients of Mg and Al in the β-Al_3Mg_2 phase (avg. composition 38 at.% Mg).

	D_{Mg}	D_{Al}
Q (kJ/mol)	100.0	111.9
D_o (m^2/s)	1.0×10^{-6}	1.6×10^{-4}

Discussion: Extrapolations to impurity diffusion coefficients

Temperature	D_{Al}^{Mg} (m²/s)	D_{Mg}^{Al} (m²/s)
400°C	4.5×10^{-15}	9.4×10^{-15}
350°C	1.3×10^{-15}	1.2×10^{-15}
300°C	1.9×10^{-16}	7.6×10^{-17}
D_o (m²/s)	3.8×10^{-7}	1.0×10^{-2}
Q (kJ/mol)	101.4	154.6

- 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.



[1] T. S. Lundy and J. F. Murdock, *J. appl. Phys.*, (1962), Vol 33, pp. 1671-73
[2] J. Combronde and G. Brebec, *Acta Metall.*, (1971), Vol. 19, pp. 1393
[3] P. G. Shewmon, *Trans. AIME*, (1956), Vol. 206, pp. 918
[4] P. G. Shewmon and F. N. Rhines, *Trans. AIME*, (1954), Vol. 250, pp. 1021
[5] S. Brennan et al. *Magnesium Technol. 2010, Proc. Symp*. pp. 537-38

Discussion: Epsilon phase formation

- 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.

[1] C. Brubaker and Z. K. Liu, *Mg. Tech.*, (2004), pp. 229-34.
[2]Y. Funamizu and K. Watanabe, *Trans. Jpn. Inst. Met.*, (1972), Vol. 13, pp.278-83
[3] G.V. Kidson, *J. Nucl. Mater.*, (1961), Vol 3 No 1, pp. 21-29.
[4] G.B. Gibbs, *J. Nucl. Mater.*, (1966), Vol 20 No 1, pp. 303-306.
[5] M. Kajihara, *Acta. Metall.*, (2004), Vol. 52, pp. 1193-1200.
[6] R. Pretorius, T.K. Marais, C.C. Theron, *Mater. Sci. Rep.*, (1993), Vol. 10, No. 1-2, pp.1-83.

Discussion: Activation energies for growth and diffusion

- 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 β-phase near the β/Al (ss) interface, suggesting Al is the faster moving constituent within the β-Al_3Mg_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 γ-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 γ/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.

[*] A. Paul et al., *Acta Mater.*, (2004), Vol. 52, pp.623-30.

Ongoing Work

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

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