

# **Mg Magnesium Technology 2011**

## **Poster Session**

***Session Chair:***

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## GROWTH KINETICS OF $\gamma$ -Al<sub>12</sub>Mg<sub>17</sub> AND $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> INTERMETALLIC PHASES IN Mg VS. Al DIFFUSION COUPLES

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### Abstract

Increasing use and development of lightweight Mg-alloys have led to the desire for more fundamental research in and understanding of Mg-based systems. As a strengthening component, Al is one of the most important and common alloying elements for Mg-alloys. In this study, solid-to-solid diffusion couple techniques were employed to examine the interdiffusion between pure Mg and Al. Diffusion anneals were carried out at 300°, 350°, and 400°C for 720, 360, and 240 hours, respectively. Optical and scanning electron microscopies (SEM) were employed to observe the formation of the intermetallics  $\gamma$ -Al<sub>12</sub>Mg<sub>17</sub> and  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub>, but not  $\epsilon$ -phase. Concentration profiles were determined using X-ray energy dispersive spectroscopy (XEDS). The growth constants and activation energies were determined for each intermetallic phase.

### Introduction

Benefits of lightweight alloys and composites in various applications including transportations and military have increased interest and research in Mg-alloys [1-5]. Accurate databases of diffusion kinetic parameters are of great value in designing and tailoring composition and microstructure of materials to achieve desired properties. Understanding of diffusion between Mg and Al is of great importance since Al is one of the primary alloying elements for Mg-alloys. In this study, we examined the interdiffusion between pure Mg and Al using solid-to-solid diffusion couples annealed at 300°C, 350°C and 400°C for 720, 360, and 240 hours, respectively. Development of phase constituents and concentration profiles were examined. In this paper, we report the thicknesses of intermetallic layers observed that were measured to determine the growth constants and activation energies. Concentration profiles from each diffusion couple have been analyzed to determine the composition- and temperature-dependent coefficients of interdiffusion, intrinsic diffusion (at the marker composition) and impurity diffusion (extrapolated), and will be published elsewhere.

### Experimental Procedure

Polycrystalline Mg (99.9%) and Al (99.99%) from SCI Engineered Materials and Alfa Aesar, respectively, were sectioned into discs, 10 mm in diameter and 2 mm in thickness. The disc specimens were metallographically polished from 600 grit SiC paper down to 1  $\mu$ m alumina using a non-oxidizing lubricant. The diffusion couples, Mg vs. Al, were then assembled with 2 mm-thick Al<sub>2</sub>O<sub>3</sub> spacers in stainless steel jigs as shown in Figure 1.

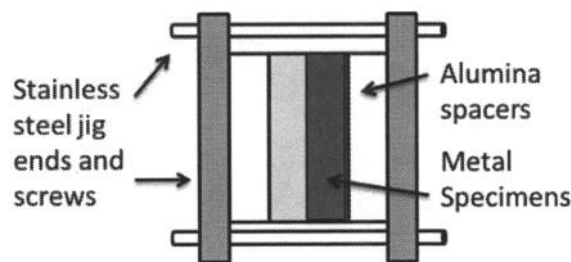


Figure 1: A schematic of Mg vs. Al diffusion couple assembly.

The jig assemblies were encapsulated individually in quartz tubes and evacuated to 10<sup>-6</sup> Torr, then backfilled with ultra-high purity argon and hydrogen mixture. The quartz capsules were placed in a Paragon Bluebird furnace that was preheated to the annealing temperature. The temperature of the diffusion couples was monitored with an independent type K thermocouple. Anneals were carried out for three diffusion couples at 300°C, 350°C and 400°C for 720, 360, and 240 hours, respectively. After the anneal, the capsules were quickly removed from the furnace and quenched in water. The entire jig and diffusion couple assembly was mounted in epoxy and cross-sectioned using a Buehler IsoMet saw with a low-speed diamond wafering blade and a non-oxidizing lubricant. The cross-sectioned specimens were then cross-mounted for metallographic preparations, again using a non-oxidizing lubricant. Each diffusion couple was examined using optical microscopy first to check the quality of the diffusion bond, then using SEM (Hitachi S-3500N) equipped with XEDS to determine the concentration profiles of each couple. The presence of surface oxides of both the Mg and Al served as the marker in these diffusion couples. The location of the Kirkendall marker plane was identified by the presence of an oxygen

X-ray peak in addition to readily-visible plane of markers on the optical micrographs. Further studies carried out also employed electron probe microanalysis (EPMA) for the determination of concentration profiles. Results from EPMA and determination of composition- and temperature-dependent coefficients of interdiffusion, intrinsic diffusion (at the marker composition) and impurity diffusion (extrapolated), and will be published elsewhere.

### Calculation of Growth Constant

To determine the diffusion growth constants for the intermediate phases that formed, a parabolic growth constant based on diffusion-controlled growth can be assumed, which is related to the thickness by:

$$Y = k\sqrt{t} \quad (1)$$

where  $Y$  is the thickness of the layer,  $k$  is the growth constant, and  $t$  is the time of anneal. The temperature dependence of the growth should follow Arrhenius relation expressed by:

$$k = k_0 \exp\left[-\frac{Q}{RT}\right] \quad (2)$$

where  $k_0$  ( $m^2/s$ ) is the pre-exponential factor,  $R$  ( $J/mol\cdot K$ ) is the gas constant,  $Q$  is the activation energy, and  $T$  is the annealing temperature in Kelvin.

### Results and Discussion

Backscatter electron micrographs from the three diffusion couples are presented in Figure 2. The concentration profiles obtained by XEDS point-to-point counting are presented in Figure 3. The micrographs and concentration profiles both clearly reveal the presence of two intermetallic layers. These two intermetallic layers correspond to  $\gamma$ - $Al_{12}Mg_{17}$  (near the Mg) and  $\beta$ - $Al_3Mg_2$  (near the Al) phases based on the concentration profiles presented in Figure 3 and the phase diagram [6] shown in Figure 4. Thicknesses measured for each phase is presented in Table I for each diffusion couple. Also presented in backscatter electron micrographs is the presence of a marker plane, identified by  $x_m$  in  $\beta$ - $Al_3Mg_2$  phase near the  $\beta/Al(ss)$  interface. A large solubility range for the  $\gamma$ - $Al_{12}Mg_{17}$  phase was observed in all couples in accordance with the phase diagram.

Table I. Thickness measured from SEM and XEDS comparison.

Phase	$\gamma$ - $Al_{12}Mg_{17}$	$\beta$ - $Al_3Mg_2$
Couple	Thickness [std. dev] ( $\mu m$ )	
400°C 10 days	226.4 [2]	595.7 [3]
350°C 15 days	77.0 [6]	481.0 [5]
300°C 30 days	29.7 [2]	272.9 [2]

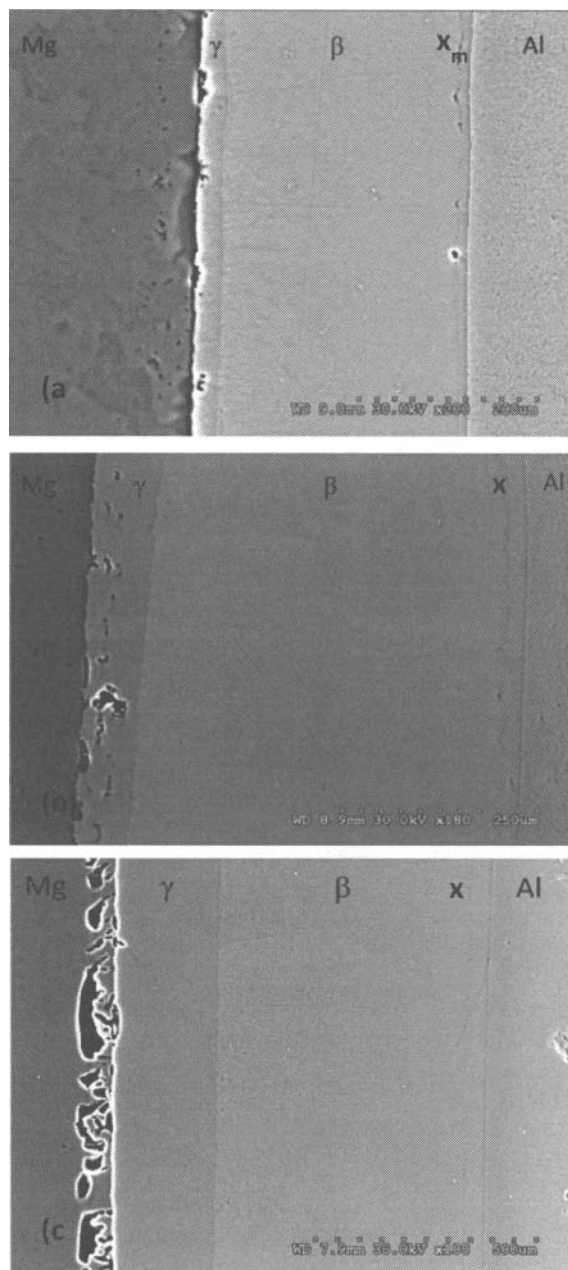


Figure 2: Backscatter electron micrographs from Mg vs. Al diffusion couples annealed at (a) 300°C for 720 hours, (b) 350°C for 360 hours, and (c) 400°C for 240 hours.

Clearly in this investigation, the  $\epsilon$ -phase did not form in any of the diffusion couples. A diffusion couple study of the Mg-Al system by Brubaker and Liu [7] in the temperature range of 360° to 420°C only gave evidence of the existence of the  $\epsilon$ -phase in diffusion couples investigated at 367° and 360°C. In contrast, an earlier investigation of the system in the range of 325° to 425°C by Funamizu and Watanabe [8] reported that the  $\epsilon$ -phase did not appear in any of the diffusion couples, which is in agreement with our current study.

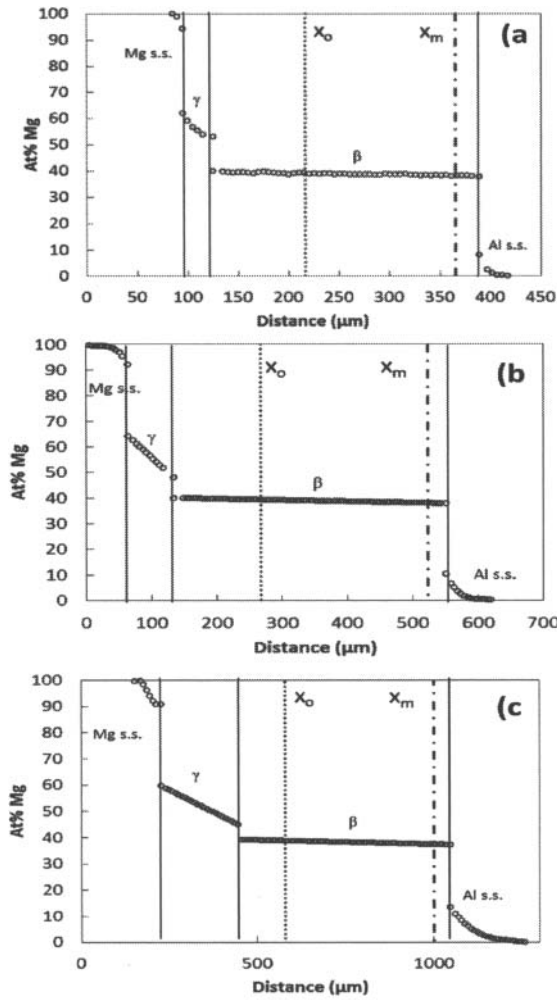


Figure 3. Concentration profiles of Mg and Al determined by XEDS from Mg vs. Al diffusion couples annealed at (a) 300°C for 720 hours, (b) 350°C for 360 hours, and (c) 400°C for 240 hours.  $X_0$  represents the Matano plane and  $X_m$  represents the marker plane.

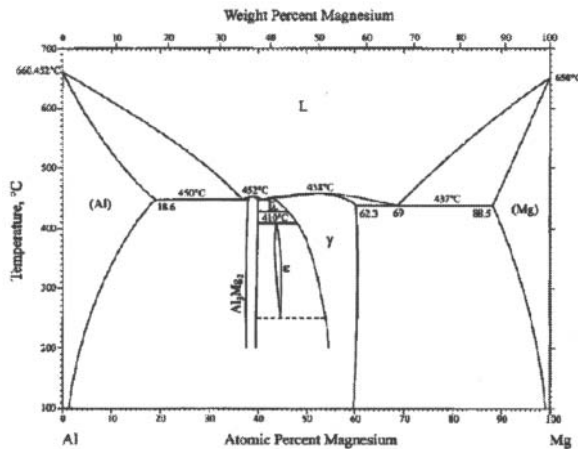


Figure 4: Al-Mg equilibrium phase diagram [6].

Table II. Activation energy and pre-exponential factor of the growth constants for  $\gamma$ - $Al_{12}Mg_{17}$  and  $\beta$ - $Al_3Mg_2$  phases.

Phase	$\gamma$ - $Al_{12}Mg_{17}$	$\beta$ - $Al_3Mg_2$
Pre-Exponential Factor, $k_0$ ( $m^2/s$ )	0.36	$2.2 \times 10^{-6}$
Activation Energy, Q (kJ/mol)	165.1	85.9
Q (kJ/mol) [7]	143.1	62.3

The growth constants, determined using Eq. (1), from the thickness measurements for the intermediate intermetallic phases,  $\gamma$ - $Al_{12}Mg_{17}$  and  $\beta$ - $Al_3Mg_2$  are plotted in an Arrhenius plot presented in Figure 5. From these plots, activation energy and pre-exponential factor for the growth constants were calculated as reported in Table II. The  $\beta$  phase with limited solubility range has the lower activation energy, and corresponds to the thicker layer observed in the diffusion couple. These results agree well with the growth constants reported by Brubaker and Liu [7]. Our activation energies for the  $\gamma$  and  $\beta$  phases are in good agreement with those reported by Funamizu and Watanabe [8].

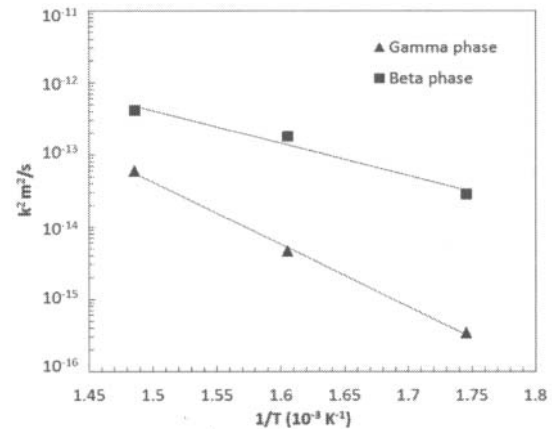


Figure 5. Temperature dependence of the growth constants in  $\gamma$ - $Al_{12}Mg_{17}$  and  $\beta$ - $Al_3Mg_2$  phases, determined from Mg vs. Al diffusion couples annealed at (a) 300°C for 720 hours, (b) 350°C for 360 hours, and (c) 400°C for 240 hours.

### Conclusions

The solid-to-solid diffusion couple technique was employed to examine intermetallic phase formation and growth in the Mg-Al system from 300°C to 400°C. SEM and XEDS were used to identify the phases present as  $\gamma$ - $Al_{12}Mg_{17}$ , and  $\beta$ - $Al_3Mg_2$ . The  $\epsilon$  phase did not appear in any of the diffusion couples studied. The pre-exponential factor and activation energy for the diffusional growth constant of each phase was calculated. The activation energy for  $\beta$ - $Al_3Mg_2$  phase growth (85.9 kJ/mole) was significantly lower than that for the  $\gamma$ - $Al_{12}Mg_{17}$  phase (165.0 kJ/mole).

### Additional Note

Based on concentration profiles measured by XEDS and EPMA, temperature and composition-dependent coefficients of interdiffusion for each phase (e.g., Boltzmann-Matano), intrinsic diffusion (marker composition and Heumann analysis) in  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> phase and impurity diffusion (extrapolated within dilute solid solutions of Mg and Al using Hall analysis) have been determined. Furthermore, corresponding activation energies and pre-exponential factors for these diffusion coefficients have been calculated. These results and relevant analyses will be published elsewhere.

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