MULTIPHASE DIFFUSION STUDY FOR Mg-Al BINARY ALLOY SYSTEM

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Abstract

Multiphase diffusion simulation and annealing experiments have been performed for Mg-Al binary alloys at various temperatures. Annealing experiments of Mg–3wt% Al and Mg–6wt% Al alloys were carried out at 330 and 400 °C for various times and the change of concentration profiles of Al in grains were measured by Electron Probe Micro Analyzer (EPMA). In order to simulate this annealing process and understand the diffusion of Mg-Al alloys, diffusion model was developed by using Finite Difference Method (FDM) coded in FORTRAN. In the diffusion simulations, composition-independent inter-diffusion coefficients were used and the intermetallic phases were assumed to have equilibrium compositions.

Introduction

Magnesium has the lowest density (two-third that of aluminum) and therefore it is a prime candidate material for use in automobiles [1]. In spite of a plenty of scopes to apply magnesium-based component in cars, the current usage is quite limited due to poor room temperature formability of Mg. Numerous researches are being carried out to improve the formability from the view point of process optimization and alloy design. Most of wrought Mg alloys are casted via ingot casting or twin roll casting route; then they are homogenized, rolled and annealed to produce Mg sheets at relative high temperature. Although these high temperature processes always involve the diffusion of alloying elements, the diffusion in multi-component Mg alloys has not been well studied. The diffusion is also important to understand creep mechanism of Mg alloys [2]. Extensive research has been performed to develop diffusion models and databases for Fe- and Ni-based alloys [3-9]. However, no systematic study has been conducted to model diffusion in Mg-based alloys. One of the reasons might be the asymmetric diffusivity in hcp-Mg. Diffusion in hcp-Mg is faster along the c-axis than the a-axis.

In order to understand and optimize the high temperature diffusion control processes of Mg alloys, fundamental and systematic diffusion studies for Mg alloys are urgently needed. In the present study, we have developed a multiphase diffusion model for Mg-Al binary alloy using the Finite Difference Method (FDM) coded in FORTRAN. Composition-independent and symmetric inter-diffusion coefficients were used for all phases and the intermetallic phases were assumed to have equilibrium compositions throughout the whole diffusion process. Annealing experiments of as-cast Mg–3wt% Al and Mg–6wt% Al alloys were carried out at 330 and 400 °C for various times and the change of Al concentration profiles in grains were measured. The diffusion of Al in randomly oriented Mg matrix was simulated using the diffusion model.

Methodology

Experimental method

Two compositions (Mg–3wt% Al and Mg–6wt% Al) were casted to observe the Al concentration profile in the hcp-Mg and β-$Mg_{17}Al_{12}$ phases. The casting was performed using a Cu plate mold (14 mm × 140 mm × 370 mm) with a cooling rate of about 80 °C/s. The casted Mg-Al binary alloy samples were then annealed at 330 and 400 °C for 1, 2, 4 and 8 h, respectively, and Al concentration profiles were examined using the Electron Probe Micro Analyzer (EPMA).

Diffusion model

A simple diffusion model was developed based on several assumptions: 1) the phase geometry is planar (one dimensional diffusion); 2) the composition at the interface is in equilibrium state; 3) the inter-diffusion coefficient of each phase is constant and 4) the diffusion in hcp-Mg is symmetric. It is well known that the diffusion in hcp-Mg is asymmetric but unfortunately no diffusivity of Al along the a- and c-axis of hcp-Mg have been determined. In the present study, as-cast dendrites (grains) showed random orientation (discussed in the Results section), so the averaged symmetric diffusivity of Al in hcp-Mg was used for the sake of simplicity.

The Finite Difference Method (FDM) is used to solve the diffusion equation, which is coded in FORTRAN. The general equation for diffusion using FDM is as follows:

$$C_i^{m,j+1} = C_i^{m,j} + \tilde{D}_p^{\ m} \frac{(\Delta t)}{(\Delta x)^2}(C_{i+1}^{m,j} - 2C_i^{m,j} + C_{i-1}^{m,j}) \quad (1)$$

where $C_{i,j}^{\ m}$ is the concentration of component m at time step j in node i (for the binary Mg-Al system, m = Mg and Al), Δt is the time step, Δx is the distance step, and $\tilde{D}_p^{\ m}$ is the inter-diffusion coefficient for component m in the p phase. Eq. (1) is the numerical solution for the diffusion equation. For the stability of the FDM approximation, Δt must be chosen with respect to the constant present in that equation. To make the FDM approximation stable, Δt is chosen according to Eq. (2):

$$2\tilde{D}_p^{\ m} \frac{\Delta t}{(\Delta x)^2} \leq 1 \quad (2)$$

In this study, we performed two kinds of simulations: single phase diffusion, to simulate the annealing process of as-cast Mg-Al alloys, and multiphase diffusion, to simulate the diffusion couple at the Mg-Al junction. In multiphase diffusion, the most important thing is to solve the moving boundary problem with consideration

of the phase transformation and nucleation at the interface. Among many different ways to solve the moving boundary problem, the Murray-Landis transformation [10] is adopted in this study. The concentration gradient was regarded as zero (zero mass transfer) at both boundaries of simulated samples. The interface compositions were determined from the Mg-Al binary equilibrium phase diagram [11] and the inter-diffusion coefficients of the various phases present in the Mg-Al system were obtained from the literature [12-16].

Results and Discussion

Annealing experiments

The variation of the Al concentration profiles between cores of two grains was examined with annealing time and temperature using EPMA. Area mapping was performed for the as-cast Mg-Al plate sample to observe local in-homogeneities throughout the whole plate in the thickness direction and also to find the overall composition of Al inside the plate. The results are reported in Fig. 1 where we can see that more scattering occurred for the Mg-6wt% Al samples than the Mg-3wt% Al ones. This is due to the fact that larger β-Mg$_{17}$Al$_{12}$ grains can be formed with higher Al concentration. Despite the scatter observed in the Al concentration data, the concentration of Al is constant throughout the samples, which means there is no significant segregation during solidification.
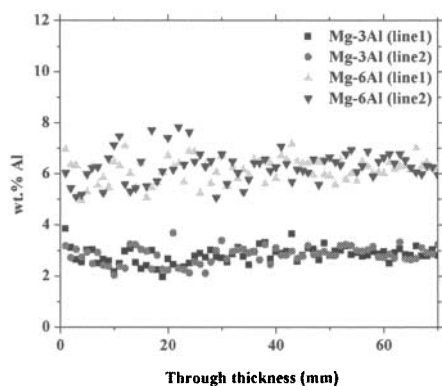

Figure 1. Area mapping results for Al concentration in Mg-3wt% Al and Mg-6wt% Al as-cast plate samples.

In order to confirm that the dendrites in as-cast samples have no preferred orientation, X-ray pole-figures were taken and presented in Fig. 2. A Bruker D8 X-ray diffraction system equipped with 2-dimentional HI-STAR detector was used to measure the texture of as-cast Mg-6wt% Al alloy. Texture measurements were done for the three main peak intensity planes for Mg which is Basal, Prismatic and Pyramidal (see Fig. 2). As seen from the pole figures, the as-cast alloy shows a random texture with no preferred orientation. As well-known, the diffusivity in hcp structure is asymmetric. To consider this asymmetric diffusion of Mg, we are studying the directional diffusivity of Mg with Mg single- and poly-crystals with different grain sizes and we will extend our diffusion model with Mg directional diffusivity in the future. For now, the present study deals with randomly oriented Mg grains (dendrites) and the averaged symmetric diffusion coefficient for Al in hcp-Mg can reasonably explain the diffusion behaviour of Al.
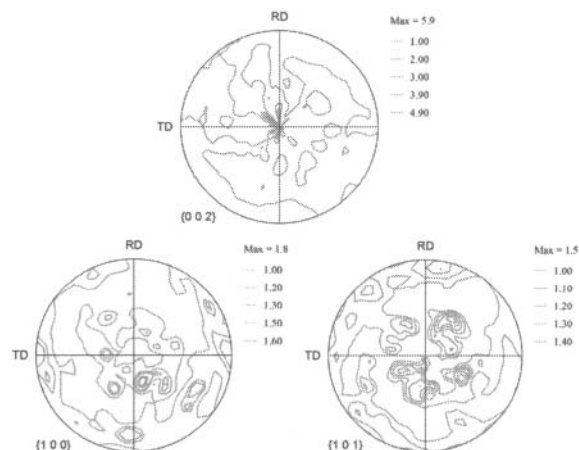

Figure 2. Pole figures of as-cast Mg-6wt%Al sample. a) Basal - (0001), b) Prism - $\{10\bar{1}0\}$ and c) Pyramidal - $\{10\bar{1}1\}$.

The as-cast microstructures (SEM image) of Mg-3wt% Al and Mg-6wt% Al alloys are presented in Fig. 3. As it can be seen, the size of the dendrites (grains) is larger than 20 μm and β-Mg$_{17}$Al$_{12}$ is dispersed around the dendrites in both alloys. In the case of Mg-3wt% Al, the size of the β phase is small (~3 μm) compared to the one (up to ~30 μm) in Mg-6wt% Al. The large β phase can be at the origin of the large scattering in the Al concentrations depicted in Fig. 1.
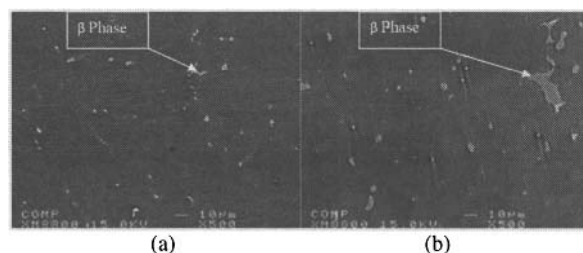

Figure 3. As-cast microstructures (SEM) of (a) Mg-3wt% Al and (b) Mg-6wt% Al. β phases were confirmed by EDS analysis.

As expected, the dendrites in as-cast samples have quite significant cored microstructure. For the Mg-6wt% Al alloy, the Al concentration at the dendrite core is about 2 wt% and reach about 8 wt% near the boundary. In order to investigate the homogenization of Al concentration in the grain, annealing of the samples was carried out at 330 and 400 °C for up to 8 h. The microstructural changes due to this annealing are presented in Fig. 4. For the Mg-3wt% Al alloy, the sample was almost fully homogenized after 8 h at 330 and 400 °C and the β phase almost vanished. In the case of Mg-6wt% Al alloy, the microstructure is almost fully homogenized at 400 °C after 8 h but not at 330 °C even after 8 h. However, some segregated area can still be observed in the Mg-6wt% Al alloy after 8 h as it can be seen in Fig. 4(d). To investigate the change of Al concentration profile across the grain during the annealing process, EPMA line-scans of Al and Mg were carried out for the as-cast and annealed samples.
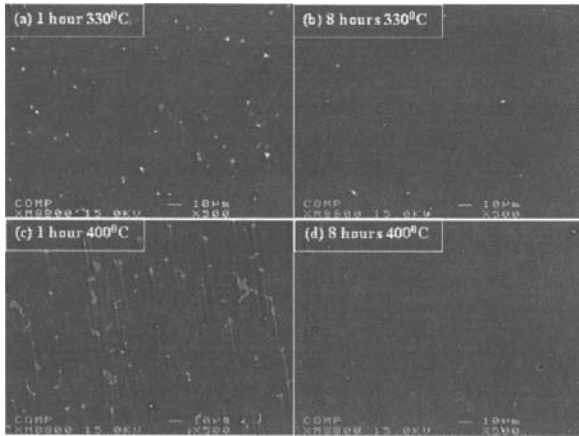
Figure 4. Microstructures of (a) and (b) Mg-3wt% Al, and (c) and (d) Mg-6wt% Al, after annealing.

To avoid the sudden change of the Al profile due to the presence of the β phase at the grain boundary, the line-scans were carefully positioned between the cores of grains through the grain boundary without crossing the β phase as shown by the bold lines in Fig. 5. In each sample, 15 randomly selected lines were scanned. The measured Al concentration profiles for Mg-6wt% Al alloy annealed at 330 and 400 °C are presented in Fig. 6. The as-cast profile shows very strong segregation of Al near the grain (dendrite) boundary. As mentioned above, the Al concentration near the grain boundary is about 8 wt%. Annealing of the sample at 330 °C for 8 h was not enough to homogenize the Al concentration in the grain. On the other hand, the Al concentration was found to be fully homogenized at 400 °C after 8h.
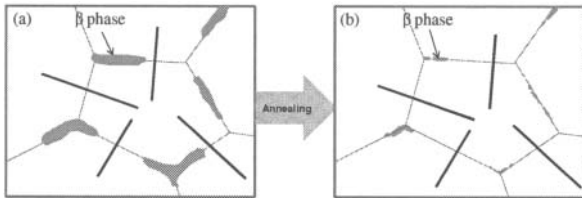

Figure 5. Schematic representation of Mg-Al binary alloy microstructure; (a) as-cast and (b) as-annealed sample (bold lines represent the position of the elemental line scans performed in the present study).

Diffusion simulation

Diffusivity of Al in hcp-Mg has been determined by several researchers [12-14] and the values are slightly different. In order to find out the reliability/accuracy of the available diffusivity data, we performed diffusion simulation for the annealing process shown in Fig. 6 using available inter-diffusion coefficients. The results are reported in Fig. 7. The as-cast concentration profile measured in the present study was used as an input for the simulation. It was also assumed that the Al profile is not influenced by the grain boundary. As the diffusivity of Abe and Onodera [13] is quite similar to that of Moreau et al. [12], we do not present their results here.
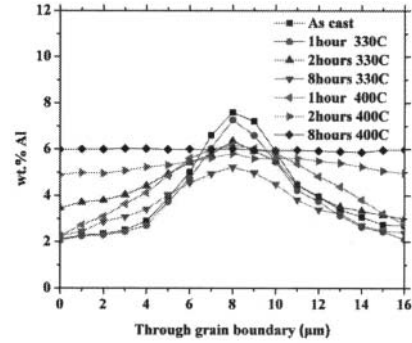

Figure 6. Change of the Al concentration profiles of Mg-6wt% Al between cores of grains (dendrites) through grain boundary with annealing time.
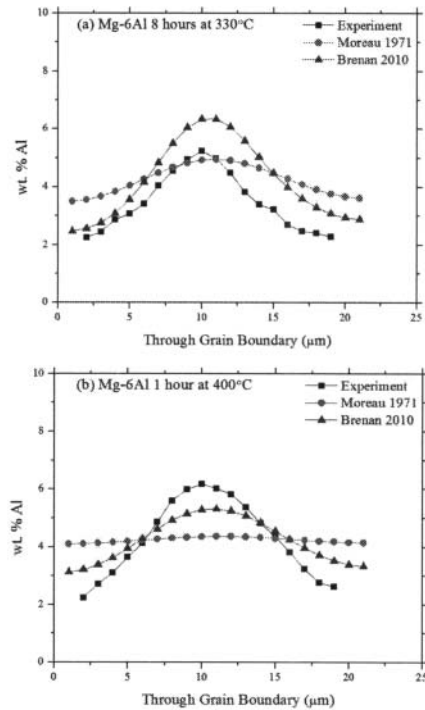

Figure 7. Calculated Al concentration profile in hcp-Mg using two available diffusion coefficients of Al from literature [12,14] in comparison with the present experimental annealing data.

After comparison of the simulation results with the experimental ones, it was found that the diffusivity reported by Moreau et al. [12] at 400 °C is too high to reproduce the experimental results (Fig. 7(b)). The simulation with the diffusivity by Moreau et al. already reached homogenization of the Al concentration at 400 °C in 1 h. On the other hand, the simulated Al profile with the diffusivity value of Brennan et al. [14] is similar to the experimental results at 400 °C in 1 h. The difference in the diffusivity values of Al at 330 °C from Moreau et al. [12] and Brennan et al. [14] is smaller than that at 400 °C (Fig. 7(a)), but the diffusivity from Moreau et al. [12] is still higher than that of

Brennan et al. [14]. The simulated Al profile at 330 °C is similar to each oher but still the results with Brennan et al. are in better agreement with the experimental annealing data. Even when the spherical geometry of the grains was considered in the diffusion simulation, the results were similar. Therefore, we found that the inter-diffusion coefficient of Al from the recent study of Brennan et al. [14] can more accurately reproduce the diffusion process for Mg-Al alloys. Using the diffusion coefficient of Al in hcp-Mg from Brennan et al. [14] and the diffusion coefficients for other phases listed in Table I, the multiphase diffusion simulation at 415 and 420 °C for 6 and 10 days, respectively, were performed and the results are presented in Fig. 8.

Table I. Inter-diffusion coefficient values for each phase in the Mg-Al binary system used in the present study.

$$\tilde{D} = D_0 \exp(-Q/RT)$$

Elements		D_0 (m/s^2)	Q (J)	Reference
Al	HCP	4.13e-3	157696	Brenan 2010
	HCP	1.20e-3	143449	Moreau 1971*
	FCC	1.41e-5	126719	Yao 2008
$Mg_{17}Al_{12}$		7.90e-5	117458	Funamizu 1972
Mg_2Al_3		3.00e-8	56848	

* This value is not used for Mg-Al multiphase diffusion simulation in the present study.
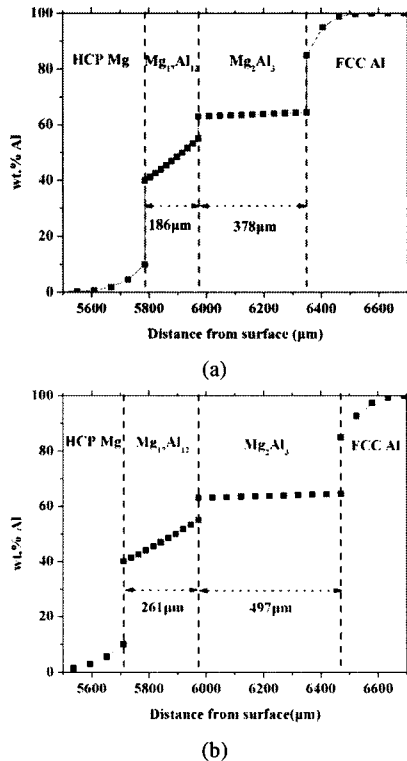

(a)

(b)

Figure 8. Calculated concentration profile of Al for Mg-Al binary diffusion couple. (a) at 415 °C for 6 days, (b) at 420 °C for 10 days.

The calculated thicknesses of intermetallic layers are compared with experimental results [17] in Table II. The calculated

thicknesses of the $Mg_{17}Al_{12}$ and Mg_2Al_3 layers as well as the Al profiles in hcp and fcc phases are well reproduced by the present simulation with the selected diffusivity data in Table I. The Al concentration profile is clearly changed with diffusion time. Both calculated and experimental results show that the layer of Mg_2Al_3 is thicker than that of $Mg_{17}Al_{12}$, which results from the higher inter-diffusion coefficient for Mg_2Al_3 compared to that for $Mg_{17}Al_{12}$.

Table II. Calculated thickness of diffusion layers for the β and γ phase compared with experimental results [17] obtained with diffusion couple.

T (°C)	Time (days)	Thickness of diffusion layer (μm)			
		Mg_2Al_3 (γ phase)		$Mg_{17}Al_{12}$ (β phase)	
		Present work	Exp.	Present work	Exp.
415	6	378	396	186	141
420	10	497	532	261	229

Summary

A multiphase diffusion simulation model is developed for Mg-Al binary alloy system by using FDM. The model is validated by simple annealing and diffusion couple experiments. In this study, simulation results are in good agreement with experimental results. The growth rate of the Mg_2Al_3 phase is faster than that of the $Mg_{17}Al_{12}$ phase. The present diffusion simulation model is generally applicable to binary diffusion couple. The results of multiphase diffusion simulation for Mg-Al diffusion couple are promising and will lead this study further to the multi-component system.

Acknowledgement

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