

DIFFUSION COUPLE INVESTIGATION OF THE Mg-Zn SYSTEM

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Keywords: Magnesium, Zinc, Diffusion, MgZn₂, Mg₂Zn₃

Abstract

Growing use and development of lightweight Mg alloys has been the catalyst for more fundamental research in Mg based material systems to be completed. Zinc is one of the most common alloying elements in Mg alloys. Phase layer growth and interdiffusion in the binary Mg-Zn system was investigated utilizing solid-to-solid diffusion couples. Anneals were carried out at 295°, 315° and 325°C for 384, 168 and 120 hours, respectively. The diffusion microstructures that developed were examined by optical and scanning electron microscopy (SEM). Concentration profiles were determined using X-ray energy dispersive spectroscopy (XEDS) and electron microprobe analysis (EPMA). The phases observed were the Mg solid solution, Mg₂Zn₁₁, MgZn₂ and Mg₂Zn₃ in all three couples as well as the high temperature, Mg₅₁Zn₂₀ phase in the 325°C couple. The MgZn₂ phase was observed to grow the thickest layer, followed by the Mg₂Zn₃ and the Mg₂Zn₁₁ phases. Parabolic growth constants were determined for each phase. Activation energies for the growth of the intermetallic phases were calculated as 105 kJ/mol for the Mg₂Zn₃ phase and 207 kJ/mol for the MgZn₂ phase.

Introduction

The drive for more lightweight performance materials has led to increasing interest in magnesium alloys for use in applications in the transportation and electronic industries due to their unique properties, especially their light weight [1-3]. Diffusion plays an important role in many material properties and phenomena such as solidification, precipitation, creep, corrosion, oxidation, etc. Reliable diffusion parameters aid in the design, optimization and

understanding of degradation of materials, and are crucial to material development. The scarcity of diffusion data in Mg based systems is the motivation behind this study.

Zn is a common alloying element in commercial Mg alloys, typically added for solid solution and precipitation strengthening. However, little data is available regarding the phase layer growth and interdiffusion behavior in the Mg-Zn binary system. An impurity diffusion study of the radioisotope ⁶⁵Zn in polycrystalline Mg was reported by Lal in 1967 [4]. Cermak and Stloukal also reported the diffusion coefficient as a function of Al concentration of ⁶⁵Zn in Mg-xAl solid solutions (x=1.77, 3.9 and 9 wt.% Al) and in the Mg alloy AZ91 as well as the diffusion of ⁶⁵Zn in polycrystalline Mg via serial section and the residual activity method [5].

Intermetallic phase formation and growth in the Mg-Zn binary system was studied using the solid diffusion couple technique at 295, 315, and 325°C for 384, 168 and 120 hours, respectively. Three diffusion couples were successfully bonded and examined via optical and scanning electron microscopies. In all three couples, the MgZn₂, Mg₂Zn₃ and Mg₂Zn₁₁ phases were identified as well as the Mg₅₁Zn₂₀ phase in the 325°C couple in accordance with the phase diagram shown in Figure 1. Parabolic growth constants were calculated for each phase and activation energies for growth were determined for the MgZn₂ and Mg₂Zn₃ phases.

Experimental Procedure

Rods of pure, polycrystalline Mg (99.9%) and pure Zn (99.9%) from Alfa AesarTM were sectioned into disks, 10 mm in diameter and 2 mm in thickness. These disk specimens were

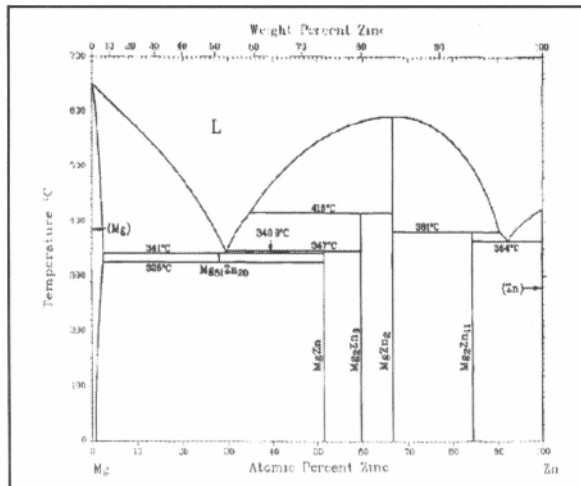


Figure 1: Mg-Zn equilibrium phase diagram [6].

then metallographically polished down to 1 μm using a non-oxidizing lubricant at each grinding and polishing step. Any contact with water was avoided during the preparation process due to the high reactivity of Mg. Mg vs. Zn diffusion couples were assembled as illustrated in Figure 2, with the polished faces of the disks touching, sandwiched between inert, Alumina (Al_2O_3) spacers and clamped in a stainless steel jig. The entire jig assembly was then placed in a quartz capsule, which is repeatedly evacuated to $\sim 10^{-6}$ torr and flushed alternately with hydrogen and ultra-high purity argon. The capsule is then backfilled with ultra-high purity argon to a pressure slightly above 1 atm at the respective annealing temperature.

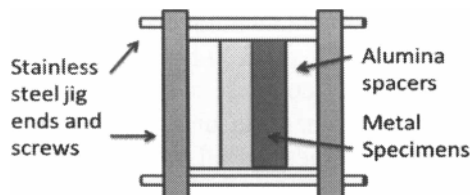


Figure 2: Schematic illustration of the diffusion couple jig assembly.

A Paragon BluebirdTM furnace was preheated to the annealing temperature, and the capsule was placed inside. The temperature was monitored with an independent type-K thermocouple and stabilized within $\pm 2^\circ$ of the desired temperature. Three diffusion couples were assembled and annealed at 295, 315, and 325°C for 384, 168 and 120 hours, respectively. After the diffusion anneal, the quartz capsule was then

quickly removed and quenched in cold water. The whole jig assembly was mounted in epoxy, cross-sectioned, and metallographically prepared for examination. OM was used to check the bond quality and field emission-SEM (Zeiss Ultra55TM) equipped with XEDS (X-ray energy dispersive spectroscopy) was utilized to identify the intermetallic phases present along with the equilibrium phase diagram presented in Figure 1. Electron micrographs of the resulting diffusion microstructures were used to measure phase thicknesses via image analysis. Parabolic growth constants, k_p , were determined for each phase as described by the equation [7]:

$$k_p = \frac{Y^2}{t} \quad (1)$$

where Y is the layer thickness measured, and t is the annealing time. Activation energy for growth of a phase, Q_k , was determined using the relation:

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

where k_0 is the pre-exponential factor, R is the ideal gas constant (8.314 J/mol-K) and T is the absolute annealing temperature.

Results

Diffusion Microstructures

Figure 3 shows electron micrographs of the resulting diffusion microstructures for each temperature studied. In all three diffusion couples the MgZn_2 , Mg_2Zn_3 , and $\text{Mg}_2\text{Zn}_{11}$ phases were identified, and the $\text{Mg}_{51}\text{Zn}_{20}$ phase was found in the 325°C diffusion couple. The MgZn phase was not observed in any of the diffusion couples studied. The $\text{Mg}_2\text{Zn}_{11}$ phase is extremely brittle, resulting in the pullout of the phase in the thin layer seen in Figure 3a in the 295°C couple. A small amount of the native oxide layers on both the Mg and Zn disks were present on the surfaces of both disks and served as markers in these experiments. Evidence of this can be seen clearly in the 315 and 325°C couples, where the original interface, or marker plane, is identified in the $\text{Mg}_2\text{Zn}_{11}$ phase.

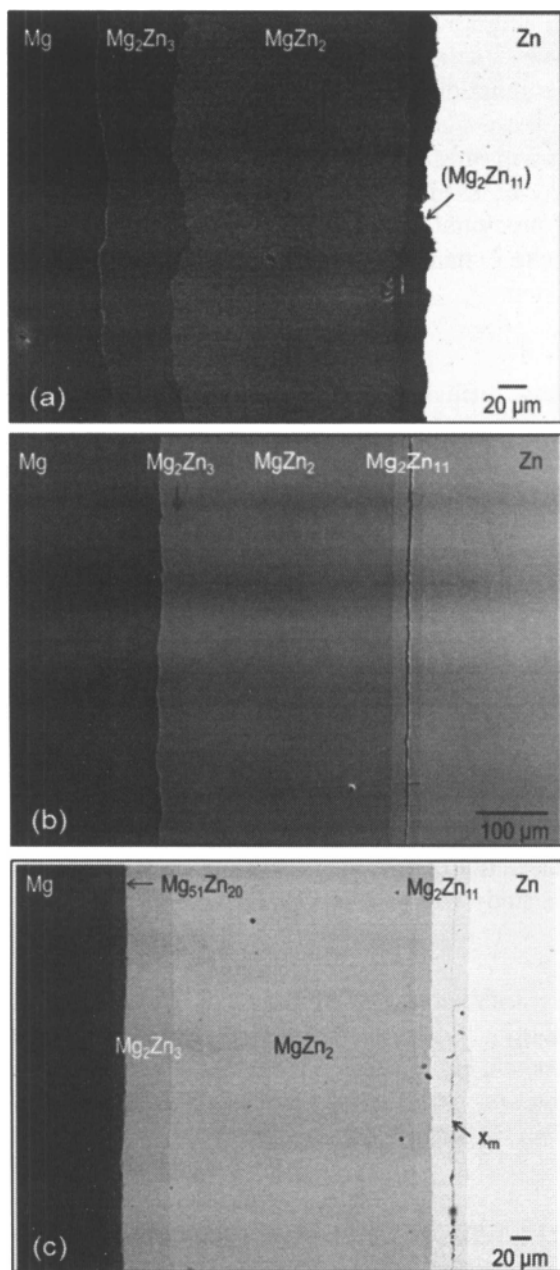


Figure 3: Representative electron micrographs of microstructure from Mg vs. Zn diffusion couple annealed at (a) 295°C for 384 hours, (b) 315°C for 168 hours, and (c) 325°C for 120 hours. X_m is the marker plane. (Note: Mg_2Zn_{11} in (a) is mostly pulled out from the diffusion couple).

Growth Constants and Activation Energies

A minimum of 15 random-location measurements was made to determine the thickness of each phase present in each diffusion couple using image analysis. Parabolic growth constants were calculated using Eq. [1], and are

reported along with the thickness measurements in Table I. Figure 4 displays the temperature-dependence of the growth constants for the Mg_2Zn_3 and $MgZn_2$ phases. $MgZn_2$ grew thicker, as evident in the above micrographs and the thickness measurements in Table I, and has the correspondingly higher parabolic growth constants. The phase diagram in Figure 1 shows that the $MgZn_2$ phase has the highest melting point of the intermetallic phases present in this binary system and is therefore more thermodynamically stable.

Table I: Intermetallic phase layer thicknesses, Y , and parabolic growth constants, k_p .

Couple	Mg_2Zn_3		$MgZn_2$	
	Y (μm) [SD]	k_p (m^2/s)	Y (μm) [SD]	k_p (m^2/s)
295°C 384 hr.	45.0 [4.1]	7.3×10^{-16}	157.0 [3.4]	9.0×10^{-15}
315°C 168 hr.	37.3 [1.4]	1.1×10^{-15}	244.6 [1.6]	4.9×10^{-14}
325°C 120 hr.	45.7 [1.1]	2.4×10^{-15}	258.0 [1.7]	7.7×10^{-14}
Couple	Mg_2Zn_{11}		$Mg_{51}Zn_{20}$	
	Y (μm) [SD]	k_p (m^2/s)	Y (μm) [SD]	k_p (m^2/s)
295°C 384 hr.	-	-	-	-
315°C 168 hr.	38.0 [1.0]	1.2×10^{-15}	-	-
325°C 120 hr.	36.2 [1.1]	1.5×10^{-15}	11.6 [0.8]	1.6×10^{-16}

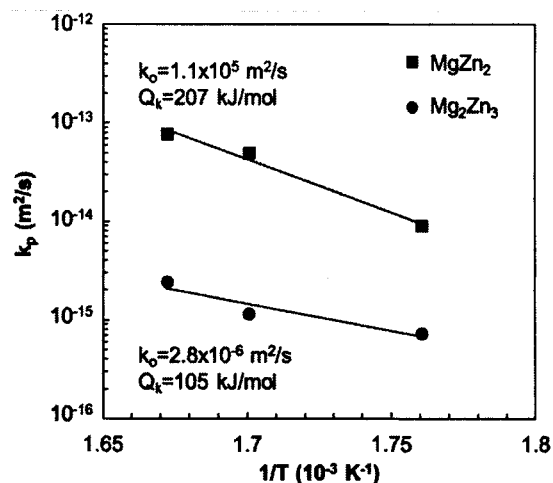


Figure 4: Arrhenius temperature-dependence of the parabolic growth constants for $MgZn_2$ and Mg_2Zn_3 intermetallic phases.

Discussion

In all three of the diffusion couples studied, the MgZn phase was not observed and the MgZn₂ Laves phase was observed to grow the thickest layer. These two observations may be explained by some fundamental guidelines of growth and diffusion theory. In general, as shown by a number of previous studies [8-11], an intermetallic phase layer will grow thicker if:

- The phase has a wider homogeneity range,
- The phase has a higher diffusion coefficient than its surrounding phases,
- The phase has a higher heat of formation (or higher melting temperature),
- The crystal structures of the adjoining phases are similar.

Both the Mg₂Zn₃ and MgZn₂ phases are stoichiometric line compounds according to the equilibrium phase diagram given in Figure 1, therefore the first guideline is not applicable. Also, the crystal structures of each phase in this binary system are dissimilar. The MgZn₂ phase has a higher melting temperature and thus is possibly more thermodynamically favorable to form. Its larger thickness and strict following of the parabolic growth law suggests the growth of the phase is diffusion controlled, and therefore has a larger diffusion coefficient than its surrounding phases. The MgZn, on the other hand, not having grown to an observable level, should have a significantly lower diffusion coefficient than its surrounding phases.

The location of the marker plane, x_m , as denoted in Figure 3, may give insight into the intrinsic diffusion behavior of the elemental species in this binary system. The marker plane is located in the Mg₂Zn₁₁ phase, near the Zn side of the diffusion couple. This suggests Zn is the faster diffusing species in the system. It is somewhat typically observed that the species with the lower melting temperature diffuses faster. Zn melts at ~420°C and Mg melts at 650°C, concluding this observation holds true for this system. Zn is well known to have a high vapor pressure as well.

Zn additions to Mg alloys are mainly added for their solid solution strengthening and precipitation strengthening. The main precipitate in these age hardenable alloys is MgZn₂. The growth rates for this phase reported in this study may be used to determine the fractional amount of precipitates and time required to achieve the desired hardening response in these alloys systems.

Summary

Three diffusion couples of pure Mg vs. pure Zn were assembled and annealed at 295, 315, and 325°C for 384, 168, and 120 hours, respectively. Intermetallic phase formation and growth for the binary system were observed. The MgZn₂, Mg₂Zn₃, and Mg₂Zn₁₁ phases were identified in all three couples as well as the Mg₅₁Zn₂₀ phase in the 325°C couple. Parabolic growth constants were determined for each phase at each temperature with MgZn₂ having the highest growth rates, followed by the Mg₂Zn₃ phase and the Mg₂Zn₁₁ phase. The activation energy for growth was calculated as 105 kJ/mole for the Mg₂Zn₃ phase and 207 kJ/mole for the MgZn₂ phase. Integrated interdiffusion coefficients for this study will be reported elsewhere.

Acknowledgments

Research sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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