Interdiffusion and Impurity Diffusion in Polycrystalline Mg Solid Solution with Al or Zn

C.C. Kammerer¹, N. Kulkarni², B. Warmack², Y.H. Sohn^{*1}

¹University of Central Florida, Advanced Materials Processing and Analysis Center

Department of Materials Science and Engineering, Orlando, FL, 32816, USA

²Oak Ridge National Laboratory, Measurement Science & Systems Engineering Division

Oak Ridge, TN, 37831, USA

* Corresponding author

Abstract

Interdiffusion and impurity diffusion in Mg binary solid solutions, Mg(Al) and Mg(Zn) were investigated at temperatures ranging from 623 to 723K. Interdiffusion coefficients were determined via the Boltzmann-Matano Method using solid-to-solid diffusion couples assembled with polycrystalline Mg and Mg(Al) or Mg(Zn) solid solutions. In addition, the Hall Method was employed to extrapolate the impurity diffusion coefficients of Al and Zn in pure polycrystalline Mg. For all diffusion couples, electron microprobe analysis was utilized for the measurement of concentration profiles. The interdiffusion coefficient in Mg(Zn) was higher than that of Mg(Al) by an order of magnitude. Additionally, the interdiffusion coefficient increased significantly as a function of Al content in Mg(Al) solid solution, but very little with Zn content in Mg(Zn) solid solution. The activation energy and pre-exponential factor for the average effective interdiffusion coefficient in Mg(Al) solid solution were determined to be $186.8 (\pm 0.9)$ kJ/mol and $7.69 \times 10^{-1} (\pm 1.80 \times 10^{-1})$ m²/sec, respectively, while those determined for Mg(Zn) solid solution were $139.5 (\pm 4.0)$ kJ/mol and $1.48 \times 10^{-3} (\pm 1.13 \times 10^{-3})$ m²/sec. In Mg, the Zn impurity diffusion coefficient was an order of magnitude higher than the Al impurity diffusion coefficient. The activation energy and pre-exponential factor for diffusion of Al impurity in Mg were determined to be $139.3 (\pm 14.8)$ kJ/mol and $6.25 \times 10^{-5} (\pm 5.37 \times 10^{-4})$ m²/sec, respectively, while those for diffusion of Zn impurity in Mg were determined to be $118.6 (\pm 6.3)$ kJ/mol and $2.90 \times 10^{-5} (\pm 4.41 \times 10^{-5})$ m²/sec.

I. Introduction

Magnesium, being lightweight, offers potential to be developed for extensive structural applications. The transportation segment has particular interest in Mg alloys for applications where reduced vehicle weight is proportional to increased fuel efficiency^[1-3]. Already, Mg alloys have been integrated into numerous automotive and aerospace applications but, because of the poor cold formability inherent of the HCP crystal structure, the vast majority is in the form of high pressure die castings^[4-5]. However, cast Mg alloys can be susceptible to porosity and, with limited thermal treatments options, may not be able to provide sufficient mechanical properties for a wider range of applications^[6-7]. Enhancing the forming characteristics of wrought Mg alloys through control of solid solution alloying and precipitation transformations can be considered paramount to fully exploit Mg alloys in lightweighting structural applications^[3, 7].

Aluminum and zinc are two of the most common alloying elements in commercial Mg alloys. They can improve the **mechanical** properties of Mg through solid solution strengthening and precipitation hardening. With the alloying addition, understanding of diffusion becomes important to kinetics of and microstructural development during solidification and heat treatment. A compilation of diffusion parameters for Mg self-diffusion and impurity diffusion in Mg was published in 2009 by Neumann and Tuijn^[8]. Similarly, a review of diffusion in metals, inclusive of interdiffusion with Mg, was released in 2004^[9]. Nonetheless, there is limited diffusion data available for Mg and Mg alloys. For example, because Al is mono-isotopic, impurity diffusion data for Al in Mg alloy is rarely available. Interdiffusion in Mg solid solution with Zn also does not exist in literature. The objective of this study was two-fold: first, is the examination of interdiffusion within the Mg solid solution phase in the binary Mg-Al and Mg-Zn

systems; second, is to extend analytical methods to determine impurity diffusion coefficients of Al and Zn in pure polycrystalline Mg. Through this investigation we determine inter- and impurity diffusion coefficients at temperatures ranging from 623 to 723K.

II. Analytical Framework

II.1. Boltzmann-Matano Analysis

In a binary solid-to-solid diffusion couple, the chemical composition varies in the interdiffusion zone. Therefore, diffusing species continuously experience different chemical surroundings and, because the diffusion coefficient will depend on concentration, it too will vary through the zone^[10]. For such systems, Boltzmann^[11] and Matano^[12] derived an integro-differential equation to calculate the interdiffusion at any given composition when molar volume variation is negligible, expressed by:

$$\tilde{D} = - \frac{\frac{1}{2t} \int_{C^{+\infty}}^{C^0} (x - x_o) dC}{\frac{\partial C}{\partial x}} \quad [1]$$

where $C^{-\infty}$ and $C^{+\infty}$ refer to the composition at terminal ends of the diffusion couple, x_o is the position of the Matano plane, and C^0 is the composition at the Matano plane. The Matano plane denotes the location of mass balance such that:

$$\int_{C^{+\infty}}^{C^0} x dC + \int_{C^0}^{C^{-\infty}} x dC = 0 \quad [2]$$

The numerator of Equation [1] is the interdiffusion flux, often expressed by:

$$\tilde{J} = \frac{1}{2t} \int_{C^{\pm\infty}}^{C^o} (x - x_o) dC \quad [3]$$

when the molar volume variation can be ignored, for example, in a single solid solution with small solubility limit, which is the case for this study.

The interdiffusion coefficient typically varies over the composition range. Therefore, Dayananda^[13] proposed an average effective interdiffusion coefficient which provides a single nominal coefficient for the compositional spectrum, and allows for comparison with other “constant” diffusion coefficients as a function of temperature. Integrating the interdiffusion flux over an interval from x_1 to x_2 , and dividing by the change in composition over the interval, yields the average effective interdiffusion coefficient, as:

$$\tilde{D}^{eff} = \frac{\int_{x_1}^{x_2} \tilde{J} dx}{(C_{x_2} - C_{x_1})} \quad [4]$$

Tracer diffusion is typically investigated with isotopic tracers of solute atoms, and the tracer diffusion coefficient is determined from the concentration profiles measured as the penetration into the substrate of a tracer solute thin film after exposure to diffusion anneals. Impurity diffusion coefficients, in cases when the suitable isotopic tracers are challenging to work with, can also be determined using the same procedure. The Darken-Manning equation^[14]

incorporates the thermodynamic factor, Φ , and vacancy-wind factor, S , to correlate the interdiffusion coefficient to tracer diffusion coefficients, D_i^* , given as:

$$\tilde{D} = (X_A D_B^* + X_B D_A^*) \Phi S \quad [5]$$

where X_A and X_B are the atomic fractions of the components, for example A and B in the binary system. In consideration of the Darken-Manning formalism, when the concentration of the solute goes to zero, both the thermodynamic and vacancy-wind factor can be ignored. Thus, the interdiffusion coefficient can be equated to a tracer diffusion coefficient of an infinitely dilute solute concentration in binary systems. However, at dilute compositional extremes, the Boltzmann-Matano Method may fail to provide adequate resolution to ascertain reliable interdiffusion coefficients and subsequent extrapolation to tracer or impurity diffusion coefficients.

II.2. Hall Method

In a typical concentration **profile** obtained in solid-to-solid diffusion couples, the concentration gradient, $\partial C/\partial x$ is difficult to determine as the composition approaches that of the terminal ends because its change becomes infinitesimally small. As illustrated in Figure 1, da Silva and Mehl^[15] utilized a semi-probability plot of concentration data to qualitatively eliminate outliers and then re-plotted the concentration profile on a linear scale to analyze using the conventional Boltzmann-Matano formalism. Since time is fixed for a given experiment, **the** probability plot of the concentration distribution **versus the Boltzmann parameter**, $l = x/2\sqrt{t}$,

yields a straight line at low concentrations as illustrated in Figure 1. In consideration of da Silva and Mehls' probability plot, Hall^[16] proposed an analytical solution using the slope and intercepts of the straight line to calculate the diffusion coefficient. Thus, the Hall Method puts the concentration gradient in terms of a Gaussian probability distribution permitting the determination of the “constant” diffusion coefficient at impurity levels. The basis of this method lies in acknowledging C/C^∞ as a probability, writing it in terms of the standard normal cumulative distribution function or:

$$\frac{C}{C^\infty} = \frac{1}{2} + \frac{1}{2} \operatorname{erf}(u) \quad [6]$$

where

$$u = h \left[\frac{x}{2\sqrt{t}} \right] + k \quad [7]$$

In order to calculate the value of u , the inverse of the standard normal cumulative distribution function, or the *Z-score*, must be calculated at each concentration probability. The *Z-score* is the upper bound of the cumulative distribution function and is proportional to the u parameter. The u parameter is linear at low concentrations when plotted against the Boltzmann variable. The slope, h , and intercept, k , of this straight line are determined with a least squares linear regression model. As a result, the diffusion equation^[17] can be rewritten in terms of h , k , and u such that:

$$D = \frac{1}{h^2} + \frac{k\sqrt{\pi}}{h^2} [1 - \operatorname{erf}(u)] \exp[u^2] \quad [8]$$

However, this method also has limitations. The concentration profile is expected to conform to the probability density function, which has an error function solution. Not all concentration profiles satisfy the error function in its entirety. Therefore, the validity of the Hall Method is limited to the linear portion of the probability plot, which is, as previously stated, present at low concentration; its applicability diminishes as the changes in concentration increases. The accuracy of the Hall Method to determine impurity diffusion coefficients can be corroborated by comparing the extrapolated impurity diffusion coefficient with tracer diffusion coefficients.

III. Experimental Procedures

Binary solid solution Mg alloys, Mg-9wt.%Al (MA9) and Mg-6wt.%Zn (MZ6), were coupled to pure Mg to gain insight into the concentration dependent interdiffusion and impurity diffusion of Al and Zn in Mg. The pure Mg (Polycrystalline, 99.9%) was commercially procured from Alfa Aesar, while the Mg alloys were produced by Magnesium Elektron (Madison, IL, USA). The chemical analysis for the pure Mg and Mg alloys is presented in Table I. The alloys were cast into roughly 40 mm diameter billets, 100 mm in length. The billets were scalped, removing the outer contaminated skin, and preheated in an inert atmosphere at 673K for one hour prior to extrusion. The extruded rod had a final diameter of 9mm. The pure Mg rods and extruded Mg alloy rods were subjected to a homogenization/grain-growth anneal roughly 40 – 50K below its respective solidus for 8 – 16 hours. The grain **sizes** of the all the Mg and Mg

alloys employed in this investigation range from 100 to 500 μ m. The rods were sectioned into discs of 3 – 4 mm in thickness and 8 – 9 mm in diameter.

The discs were prepared for diffusion experiments by incrementally polishing the surface down to 1 μ m using ethyl alcohol as a non-oxidizing lubricant. An intimate interface between two or more discs was achieved with the aid of a 317L steel assembly jig consisting of two steel plates pulled together with three screws. Alumina spacers were placed between the steel plates and sample discs to inhibit diffusion bonding of the steel to the sample discs. The loaded jig was placed in a quartz ampoule and a quartz cap was welded onto the open end of the ampoule using standard flame-working techniques. The stem of the ampoule was attached to a vacuum system capable of pulling vacuum to $\sim 10^{-9}$ atm (10^{-6} Torr) as well as injecting hydrogen or argon gas. The ampoule was evacuated and flushed with hydrogen and ultra-high purity argon several times, and then fully evacuated to $\sim 10^{-9}$ atm before the stem was removed from the capsule. A photograph of a typical encapsulated diffusion couple assembly along with a schematic of the assembled jig is shown in Figure 2.

The encapsulated assemblies were instrumented with calibrated resistance temperature detectors (RTD). The RTDs accurately correlate the resistance across the sheathed element with temperature. The instrumented capsule was placed in either a Paragon Bluebird™ furnace or a Lindberg™ three-zone tube furnace preheated to the annealing temperature. The temperature of the diffusion couples was monitored via the independent RTD probe through an Omega™ data acquisition system. Each diffusion couple system was annealed at three different temperatures. Temperature was controlled within ± 2 K of the set point. Diffusion anneal temperatures and times are detailed in Table II. After annealing, the capsule was quickly removed from the furnace and quenched in water at room temperature. The couple was extracted from the jig and cold

mounted in epoxy. Once cured, the couple was cross-sectioned and metallographically prepared down to 1 μ m finish, again using non-oxidizing lubricants.

Each diffusion couple was first examined using optical microscopy to check the diffusion bond integrity. A Field Emission Scanning Electron Microscope equipped with an X-ray Energy Dispersive Spectrometer (Zeiss Ultra 55 FE-SEM with XEDS) was used to further check the diffusion bond integrity and to approximate the thickness wherein interdiffusion had occurred ($\partial C/\partial x \neq 0$). **Electron Probe Microanalysis (JEOL JXA-8200 EPMA)** was used for quantitative chemical analysis of the concentration profiles. EPMA allowed for precise compositional determination across the diffusion zone. **In order to improve the accuracy and have an understanding of uncertainty for the subsequent analysis, multiple EPMA line scans were collected and analyzed for each diffusion couple.** Line scans were performed on the central region of each bonded couple and orthogonal to the interface extending approximately 50 μ m beyond where the concentration gradient became negligible ($\partial C/\partial x = 0$). Measured x-ray intensities were corrected for matrix effects by applying the Heinrich ZAF correction factors. Pure Mg and Mg-alloy standards were used for equipment calibration. Typical operating conditions were 7.5 keV accelerating voltage for Mg vs. MA9 and 15 keV for Mg vs. MZ6; probe current was 50 nA. **The step size of the EPMA line scan was varied by couple, between 2 μ m and 10 μ m, depending on the thickness of the interdiffusion zone.**

Concentration profiles determined by EPMA were fitted using piecewise cubic smoothing splines that are continuous up to a **second** order derivative. Each piecewise spline used to fit the concentration profiles in this study typically represented 4 to 10 evenly spaced EPMA data points. As a result, each concentration profile consists of 10 to 40 piecewise cubic splines. **The goodness of fit can be quantified as the mean squared error (MSE), which represents**

the composition difference between the EPMA data and fitted profile. A concentration profile with the largest EPMA scatter observed in this investigation is presented in Figure 3 along with the curve fit employed for the subsequent analyses. The MSE for this data set is $0.003 \text{ (at.\%)}^2$; the square root of the MSE can be viewed as the standard deviation of the fit and is 0.06 at.%. Therefore the curve fits represent the actual concentration profiles within 0.1 at.% given a 95% confidence interval.

On the basis of the Boltzmann-Matano analysis, composition-dependent interdiffusion coefficients in Mg(Al) and Mg(Zn) solid solutions were calculated using Equation [1], and the average effective interdiffusion coefficients were calculated using Equation [4]. Diffusion theory and the semi-infinite boundary condition employed in this study dictate the concentration at the Matano plane should be consistent between individual EPMA line scans of the same couple. Experimental and analytical factors can introduce error. Therefore, to ensure integrity of the diffusion data generated, EPMA line scans which yielded anomalous Matano compositions and/or terminal compositions were excluded from the Boltzmann-Matano analysis.

Using the Hall Method, Al and Zn impurity diffusion coefficients in pure polycrystalline Mg were calculated using Equation [8]. For diffusion coefficients reported in this study, individual from each EPMA line scan, average, and standard deviations are reported. The activation energy and pre-exponential factor was determined from an exponential least squares fit of the average for the diffusion coefficients as a function of inverse temperature (i.e. Arrhenius relationship). The tolerances were computed from the propagation of the standard deviation into the least squares fit.

IV. Results

IV.1. Interdiffusion and Impurity Diffusion in Mg(Al) Solid Solution

Three EPMA line scans were collected for each of the couples annealed at 623K and 723K; at 673K, only two line scans through the interdiffusion zone were collected. At 623K and 723K, one line scan yielded an anomalous Matano composition and was excluded from Boltzmann-Matano analysis. In the case of the couple annealed at 623 K, an adequate fit could not be achieved throughout the entire composition profile for one of the line scans; this line scan was also excluded from the subsequent Boltzmann-Matano analysis. However all collected EPMA line scans were used for Hall Analysis.

The Boltzmann-Matano Method was used to calculate interdiffusion coefficients as a function of solute concentration. However, when the composition approaches dilution, this method of determining interdiffusion coefficients can become susceptible to increased error. Therefore, the analytical approach purported by Hall was used to determine the interdiffusion coefficient for Mg(Al) solid solution at compositions less than 1 at.% Al. The results for Mg(Al) solid solution are presented in Figure 4. There is good continuity in interdiffusion coefficients calculated using the Boltzmann-Matano Method at compositions >1 at.% Al and the Hall Method at compositions < 1 at.% Al. Figure 4 clearly indicates that the magnitude of interdiffusion coefficient increases as Al concentration increases, particularly at 673 and 723K.

The interdiffusion coefficient for specific compositions within the Mg(Al) solid solution phase was examined as a function of temperature to determine the activation energy as a function of solute concentration. Figure 5 presents the increase in activation energy with increasing Al concentration. As the concentration approaches the terminal end, determination of $\partial c/\partial x$ is increasingly difficult, and increases the uncertainty in diffusion coefficients calculated.

Furthermore, at 623 K, the equilibrium for Mg-8at.%Al is near the solvus, approaching the two-phase region. The combination of these two factors likely contributes to the divergence from the apparent trend in Figure 5.

The composition-dependent interdiffusion coefficients determined via Boltzmann-Matano analysis were averaged to an effective interdiffusion coefficient for Mg(Al) solid solution using Equation [4]. Using the Arrhenius relationship, the activation energy and pre-exponential factor were calculated for the average effective interdiffusion coefficients in Mg(Al) solid solution. These values are reported in Table III, for the composition range of 0 to 8.5 at.% Al and temperature range of 623 to 723K. The average effective interdiffusion activation energy and pre-exponential factor for Mg(Al) solid solution is $186.8 (\pm 0.9) \text{ kJ/mol}$ and $7.69 \times 10^{-1} (\pm 1.80 \times 10^{-1}) \text{ m}^2/\text{sec}$, respectively.

The implementation of the Hall Method was carried out by performing a linear regression of the semi-probability plot (i.e. concentration distribution versus Boltzmann parameter) over the composition range of 0.05 – 1.3 at.% Al. Thus the Hall interdiffusion coefficient at the infinitely dilute composition can be estimated as the impurity diffusion coefficient by extrapolating the diffusion profile to a zero concentration. The impurity diffusion coefficients for Al in Mg at 623, 673 and 723K are reported in Table IV, along with the activation energy and pre-exponential factor, determined as $139.3 (\pm 14.8) \text{ kJ/mol}$ and $6.25 \times 10^{-5} (\pm 5.37 \times 10^{-4}) \text{ m}^2/\text{sec}$, respectively.

IV.2. Interdiffusion and Impurity Diffusion in Mg(Zn) Solid Solution

Three EPMA line scans were collected for each of the couples. At 673K one line scan yielded an anomalous Matano composition and was excluded from Boltzmann-Matano analysis. All collected line scans were used for Hall Analysis.

The Boltzmann-Matano and Hall Methods were used to determine the interdiffusion coefficient for Mg(Zn) solid solution at compositions greater than and less than 0.5 at.% Zn, respectively. The interdiffusion coefficients are presented as a function of Zn concentration Figure 6. Compared to that of the Al in Mg solid solution, the magnitude of interdiffusion coefficients of Zn in the Mg solid solution is higher. Also, the interdiffusion coefficients of Zn in Mg solid solution are relatively unchanged over the composition range investigated. As was done for Mg(Al), the interdiffusion coefficient for specific compositions within the Mg(Zn) solid solution phase was examined as a function of temperature to reveal the concentration dependence of the activation energy for interdiffusion. These results are presented in Figure 5; it can be seen that the activation energy increases slightly.

Using Eq. [4], average effective interdiffusion coefficients for the Mg(Zn) solid solution with Zn concentration from 0 to 2 at.% were determined at 623, 673, and 723K. From the Arrhenius relationship, the activation energy and pre-exponential factor for the average effective interdiffusion coefficient were calculated for the Mg(Zn) solid solution. The average effective interdiffusion coefficient, pre-exponential factor, and activation energy, presented in Table V, are valid between 0 at.% and 2.0 at.% Zn. From this data, the average effective interdiffusion activation energy and pre-exponential factor for Mg(Zn) solid solution was determined to be $139.5 (\pm 4.0)$ kJ/mol and $1.48 \times 10^{-3} (\pm 1.13 \times 10^{-3})$ m²/sec, respectively.

The implementation of the Hall Method was carried out by performing a linear regression of the semi-probability plot over the composition range of 0.05 – 0.80 at.% Zn. The Hall interdiffusion coefficient at the infinitely dilute composition was ascertained by extrapolating the diffusion profile to a zero concentration, and the activation energy and pre-exponential factor of the Zn impurity diffusion in Mg was calculated, reported in Table VI. The activation energy was

determined to be $118.6 (\pm 6.3)$ kJ/mol and the pre-exponential factor was found to be 2.90×10^{-5} ($\pm 4.41 \times 10^{-5}$) m²/sec for the impurity diffusion coefficient of Zn in pure polycrystalline Mg.

V. Discussion

Figure 7 presents the temperature-dependence of the average effective interdiffusion coefficient for Mg(Al) and Mg(Zn) solid solution along with constant interdiffusion coefficient experimentally determined by others. For the Mg(Al) solid solution, there is good agreement with recently published work by Brennan^[18] while the activation energy appears to be higher than that determined by Moreau^[19]. However, a close examination of the Moreau's work revealed that the reported values are valid over the compositional range of 0 to 20 at.% Al, well beyond the solubility limit of Al in Mg, which is, at maximum, 12 at.% Al.

Interdiffusion data for Mg solid solution with Zn does not exist in literature. Figure 7 clearly shows that the interdiffusion coefficients in Mg(Zn) solid solution are larger than those in Mg(Al) solid solution. The activation energy for the Mg(Al) solid solution is roughly 33% higher than the activation energy for the Mg(Zn) solid solution while the pre-exponential factor for Mg(Zn) solid solution is significantly lower than that for Mg(Al) solid solution.

The impurity diffusion coefficient of Al in pure Mg is plotted as a function of temperature in Figure 8. Figure 8 also includes the Al impurity diffusion coefficient in polycrystalline Mg measured by Brennan^[20] using thin film techniques, those extrapolated from interdiffusion coefficient in single crystal Mg determined by Das^[21, 22] using diffusion couple technique and multi-phase diffusion modeling, and those in single crystal Mg calculated by Ganeshan^[23] using the 8-frequency model. The Al impurity diffusion coefficients measured by

Das^[21, 22] using single crystal Mg are similar to the those measured by thin film technique using polycrystalline Mg by Brennan^[20]. However, in the paper by Brennan, the authors have strongly acknowledged that the refined polycrystalline microstructure and depth profiling methodology employed resulted in a broadening of the diffusion profile, which led to somewhat inflated impurity diffusion coefficients^[20]. Thus, in this study, as expected, the Al impurity diffusion coefficients in polycrystalline Mg are slightly lower than those previously published by Brennan^[20]. The activation energy for Al impurity diffusion in Mg determined by the Hall Method agrees well with that determined from first-principles. On the other hand, the pre-exponential factor differs by an order of magnitude.

The temperature-dependence of the Zn impurity diffusion coefficient determined in this study is presented in Figure 9 along with those reported by others. Neumann^[8] summarized the tracer diffusion coefficients from isotopic tracer diffusion experiments carried out by Čermák^[24] and Lal^[25]. Ganeshan^[21] calculated Zn impurity diffusion coefficients based on first principles model, and Das^[26] extrapolated impurity diffusion coefficients from interdiffusion studies. Results of this study for the Zn impurity diffusion coefficients are close to those summarized by Neumann^[8], however with slightly lower activation energy as reported in Figure 9. The congruency in results between the isotopic tracer diffusion coefficient and the impurity diffusion coefficient reported in this study lends credence to the analytical approach to impurity diffusion coefficient measurements presented herein using the Hall Method.

Figure 10 presents the impurity diffusion coefficients for various elements in Mg along with tracer diffusion coefficients for Mg self-diffusion^[27]. The In and Fe diffusion coefficients were measured by tracer method^[28], those for Ce and La were analytically estimated from the rate of precipitate dissolution^[25], and those for Be were determined through solid-to-solid

diffusion couple experiments^[29]. Figure 10 clearly reveals Zn impurity diffusion to be faster than Mg self-diffusion, which in turn, is faster than the Al impurity diffusion, $D_{\text{Zn}}^* > D_{\text{Mg}}^* > D_{\text{Al}}^*$. These empirical findings are in conflict with the conclusions from first principles calculations which found Mg to self-diffuse faster than both Al and Zn impurities^[23]. The finding of this investigation can be supported by considering the vapor pressure of the dilute impurities. The vapor pressure of Al, Mg, and Zn calculated using the Riedel equation^[30-31] at the diffusion anneal temperatures are listed in Table VII. The saturated vapor pressure of Zn is notably higher than that of Al, and marginally higher than that of Mg.

VI. Conclusions

Composition-dependent and average effective interdiffusion coefficients were calculated using the Boltzmann-Matano analysis and Dayananda's consolidation, respectively, for Mg(Al) and Mg(Zn) solid solutions at temperatures ranging from 623 to 723K. The interdiffusion coefficient in Mg(Al) solid solution and the corresponding activation energy of interdiffusion increased with an increase in Al concentration. The activation energy and pre-exponential factor for the average effective interdiffusion coefficient in Mg(Al) solid solution was determined to be 186.8 (± 0.9) kJ/mol and 7.69×10^{-1} ($\pm 1.80 \times 10^{-1}$) m²/sec, respectively. Interdiffusion coefficient remains relatively constant as a function of composition in Mg(Zn) solid solution, however the activation energy increase slightly with an increase in Zn content. The activation energy and pre-exponential factor for the average effective interdiffusion coefficient in Mg solid solution with Zn was determined to be 139.5 (± 4.0) kJ/mol and 1.48×10^{-3} ($\pm 1.13 \times 10^{-3}$) m²/sec. Interdiffusion

coefficients in Mg(Al) solid solution was approximately an order of magnitude lower than those in Mg(Zn) solid solution for the temperature range examined in this study.

As the concentration of Al or Zn approaches the dilute ends, the Hall Method has proven to be effective to extract impurity diffusion coefficients from solid-to-solid diffusion couples. This method was validated by comparing outcomes obtained in this study through solid-to-solid diffusion couples between pure Mg and Mg(Zn) solid solution with results established through conventional impurity diffusion studies using isotopic tracers. Impurity diffusion coefficients of Al in Mg was determined to have an activation energy and pre-exponential factor of $139.3 (\pm 14.8)$ kJ/mol and $6.25 \times 10^{-5} (\pm 5.37 \times 10^{-4})$ m²/sec. Impurity diffusion coefficients of Zn in Mg was determined to have an activation energy and pre-exponential factor of $118.6 (\pm 6.3)$ kJ/mol and $2.90 \times 10^{-5} (\pm 4.41 \times 10^{-5})$ m²/sec. Zn impurity diffusion was observed to be faster than Mg self-diffusion which, in turn, was faster than the Al impurity diffusion.

VII. References

- [1] Luo, A. A., Mishra, R. K., Powel, B. R., Sachdev, A. K., Materials Science Forum, 706-709, 2012, pp. 69-82.
- [2] Easton, M., Beer, A., Barnett, M., Davies, C., Dunlop, G., Durandet, Y., Blacket, S., Hilditch, T., Beggs, P., JOM, 2008, 60(11), pp. 57-62.
- [3] Luo, A. A., International Materials Review, 2004, 49, pp. 13-30.
- [4] Luo, A. A, Journal of Magnesium and Alloys, 2013
<http://dx.doi.org/10.1016/j.jma.2013.02.002>
- [5] Edgar, R. L., Global Overview on Demand and Applications for Magnesium Alloys, in Magnesium Alloys and their Applications, Kainer, K. U., Wiley-VCH, Weinheim, 2000, pp. 1-8.

- [6] Agnew, S. R., Yoo, M. H., Horton, J. A., Texture Analysis as a Tool for Wrought Magnesium Alloy Development, in Magnesium Alloys and their Application, Kainer, K. U., Wiley-VCH, Weinheim, 2000, pp. 119-124.
- [7] Jaschik, C., Hagerkamp, H., Niemeyer, M., New Magnesium Wrought Alloys, in Magnesium Alloys and their Application, Kainer, K. U., Wiley-VCH, Weinheim, 2000, pp. 41-46.
- [8] Neumann, G., & Tuijn, C.: Self-Diffusion and Impurity Diffusion in Pure Metals. Elsevier, London, 2009, pp. 102-103.
- [9] Sohn, Y. H., 13 – Diffusion in metals, Smithells Metals Reference Book (Eighth Edition), W. F. Gale, PhD, and T. C. Totemeier, PhD, Oxford, 2004, Pages 1–120.
- [10] Mehrer, H.: Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes, Springer-Verlag, Berlin, 2007, pp. 161-177.
- [11] Boltzmann, L.: Ann. Physik und Chem. Wied., 1894, 53, 959.
- [12] Matano, C.: Japanese Journal of Physics, 1935, 8, 109.
- [13] Dayananda, M.: A Diffusion and Defect Forum, 1993, Vol 95-98, pp. 521-536.
- [14] Manning, J. R.: Diffusion Kinetics for Atoms in Crystals. Princeton: Van Nostrand, 1968.
- [15] da Silva, L. C. C., Mehl, R. F., Journal of Metals 3, 1951, 155.
- [16] Hall, L. D.: The Journal of Chemical Physics, 1953, 87-89.
- [17] Sarafianos, N.: Journal of Materials Science, 1986, 2283-2288.
- [18] Brennan, S., Bermudez, K., Kulkarni, N., & Sohn, Y. H.: Metallurgical and Materials Transactions A, 2012, 43. 11. 4043-4052.
- [19] Moreau, G.: Journal of Nuclear Materials, 1971, 38, 197.

- [20] Brennan, S., Warren, A. P., Coffey, K. R., Kulkarni, N., Todd, P., Kilmov, M., & Sohn, Y. H.: *Journal of Phase Equilibria and Diffusion*, 2012, 121-125.
- [21] Das, S. K., Kim, Y. M., Ha, T. K., Gauvin, R., Jung, I. H.: *Metallurgical and Materials Transactions A*, 2013, 44. 2539-2547.
- [22] Das, S. K., Kim, Y. M., Ha, T. K., Gauvin, R., Jung, I. H.: *Metallurgical and Materials Transactions A*, 2013, 44. 3420-3421.
- [23] Ganeshan, S., Hector Jr., L. G., & Liu, Z. -K.: *Acta Materialia*, 2011, 3214-3228.
- [24] Čermák, J., & Stoukal, I.: *Physica Status Solidi (a)*, 2006, 2386–2392.
- [25] Lal, K.: CEA Report R-3136, Saclay, 1967, p. 54.
- [26] Das, S. K., Kim, Y. M., Ha, R., Jung, I. H.: *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry*, 2013, 42. 51-58.
- [27] Shewmon, P. G., & Rhines, F. N.: *Trans. AIME*, 1954, 200, 1021.
- [28] Pavlinov, L. V., Gladyshev, A. M., & Bykov, V. N.: *Phys. Met. Metallogr.*, 1968, 26.
- [29] Yerko, V. F., Zelenskiy, V. F., & Krasnorutskiy, V. S. (1966). *Phys. Met Metallogr.*, 22(1), 112.
- [30] Alcock, C. B., Itkin, V. P., & Horrigan, M. K.: *Metallurgical Quarterly*, 1984, 309.
- [31] Vetere, A.: *Industrial & Engineering Chemistry Research*, 1991, pp. 2487-2492.

Table I: Chemical composition of pure Mg and Mg alloys

	Mg wt.% (at.%)	Al wt.% (at.%)	Zn wt.% (at.%)	Others wt.%	Each wt.%
Mg	99.95 (100.00)	0.00 (0.00)	0.00 (0.00)	<0.05	<0.002
MA9	90.38 (91.27)	9.59 (8.72)	0.016 (0.01)	<0.02	<0.005
MZ6	93.74 (97.58)	0.01 (0.01)	6.23 (2.41)	<0.02	<0.005

Table II: Diffusion anneal temperature and time parameters

Couple	Temperature (K)	Time (hours)
Mg vs. MA9	623	96
	673	17
	723	24
Mg vs. MZ6	623	125
	673	8
	723	24

Table III: Average effective interdiffusion coefficients, pre-exponential factor, and activation energy for interdiffusion in Mg(Al) solid solution, i.e., 0 to 8.5 at.% Al.

Temperature (K)	$\tilde{D}_{\text{Mg or Al}}^{\text{eff}}$ (m ² /sec)		
	Individual	Average	Standard Deviation
623K	1.38×10^{-16}	1.38×10^{-16}	--
673K	3.09×10^{-15}	3.61×10^{-15}	7.25×10^{-16}
	4.12×10^{-15}		
723K	1.95×10^{-14}	1.97×10^{-14}	2.88×10^{-16}
	1.99×10^{-14}		
D _o (m ² /sec)		0.769 ± 0.180	
Q (kJ/mole)		186.8 ± 0.9	

Table IV: Al Impurity diffusion coefficients in Mg, $D_{\text{Al}}^{\text{Mg}}$, and the corresponding pre-exponential factor and activation energy.

Temperature (K)	D ^{Mg} _{Al} (m ² /sec)		
	Individual	Average	Standard Deviation
623	8.94 x 10 ⁻¹⁷	1.32 x 10 ⁻¹⁶	3.71 x 10 ⁻¹⁷
	1.56 x 10 ⁻¹⁶		
	1.51 x 10 ⁻¹⁶		
673	1.02 x 10 ⁻¹⁵	9.54 x 10 ⁻¹⁶	9.40 x 10 ⁻¹⁷
	8.87 x 10 ⁻¹⁶		
723	4.87 x 10 ⁻¹⁵	5.45 x 10 ⁻¹⁵	5.26 x 10 ⁻¹⁶
	5.89 x 10 ⁻¹⁵		
	6.96 x 10 ⁻¹⁵		
D _o (m ² /sec)		6.25 x 10 ⁻⁵ ± 5.37 x 10 ⁻⁴	
Q (kJ/mole)		139.3 ± 14.8	

Table V: Average effective interdiffusion coefficients, pre-exponential factor, and activation energy for interdiffusion in Mg(Zn)solid solution, i.e., 0 to 2.0 at.% Zn.

Temperature (K)	$\tilde{D}_{\text{Mg or Zn}}^{\text{eff}}$ (m ² /sec)		
	Individual	Average	Standard Deviation
623K	3.03 x 10 ⁻¹⁵	2.89 x 10 ⁻¹⁵	2.40 x 10 ⁻¹⁶
	3.03 x 10 ⁻¹⁵		
	2.62 x 10 ⁻¹⁵		
673K	2.40 x 10 ⁻¹⁴	2.41 x 10 ⁻¹⁴	1.03 x 10 ⁻¹⁶
	2.41 x 10 ⁻¹⁴		
723K	1.17 x 10 ⁻¹³	1.19 x 10 ⁻¹³	2.57 x 10 ⁻¹⁵
	1.22 x 10 ⁻¹³		
	1.19 x 10 ⁻¹³		
D _o (m ² /sec)		1.48 x 10 ⁻³ ± 1.13 x 10 ⁻³	
Q (kJ/mole)		139.5 ± 4.0	

Table VI: Zn Impurity diffusion coefficients in Mg, D_{Zn}^{Mg} , and the corresponding pre-exponential factor and activation energy.

Temperature (K)	D _{Zn} ^{Mg} (m ² /sec)		
	Individual	Average	Standard Deviation
623	3.51 x 10 ⁻¹⁵	3.04 x 10 ⁻¹⁵	4.16 x 10 ⁻¹⁶
	2.91 x 10 ⁻¹⁵		
	2.71 x 10 ⁻¹⁵		
673	1.57 x 10 ⁻¹⁴	2.11 x 10 ⁻¹⁴	5.16 x 10 ⁻¹⁵
	2.15 x 10 ⁻¹⁴		
	2.60 x 10 ⁻¹⁴		
723	7.27 x 10 ⁻¹⁴	7.15 x 10 ⁻¹⁴	1.08 x 10 ⁻¹⁵
	7.07 x 10 ⁻¹⁴		
	7.10 x 10 ⁻¹⁴		
D _o (m ² /sec)		2.90 x 10 ⁻⁵ ± 4.41 x 10 ⁻⁵	
Q (kJ/mole)		118.6 ± 6.3	

Table VII: Saturated vapor pressure^[30] of Al, Mg, and Zn at the diffusion anneal temperatures

(atm)	Al	Mg	Zn
623K	2.6×10^{-21}	4.4×10^{-7}	1.7×10^{-5}
673K	2.8×10^{-19}	3.5×10^{-6}	1.1×10^{-4}
723K	1.6×10^{-17}	2.1×10^{-5}	5.4×10^{-4}

List of Figures

1. Probability plot of C/C_0 vs. the Boltzmann parameter, λ for Cu – Ni at 1054°C ($C_0=100\%$; $C=C_{Cu}$; $t=1.12 \times 10^6$ sec). Data of da Silva and Mehl,^[15] Redrawn from Hall.^[16]
2. Encapsulated diffusion couple assembly with a schematic illustration of assembled jig.
3. A concentration profile of Zn determined by EPMA from Mg vs. MZ6 diffusion couple annealed at 623K for 125 hours. Concentration profile determined by EPMA is indicated by open circles, and fitted one with piecewise cubic smoothing spline is indicated by solid line. The scatter in EPMA presented is the largest observed in this study. The fitted concentration profile represents the actual concentration profiles within 0.1 at.% given a 95% confidence interval.
4. Interdiffusion coefficients as a function of Al composition determined using the Boltzmann-Matano method at compositions >1 at.% Al and the analytical Hall method at composition < 1 at.% Al.
5. Variation in activation energy of interdiffusion as a function of solute concentration in Mg(Al) and Mg(Zn) solid solution.
6. Interdiffusion coefficients in the Mg rich solid solution of the Mg-Zn binary system. The demarcation separates the analysis based on the Hall method and that based on the Boltzmann-Matano method.
7. Average effective interdiffusion coefficient of Mg solid solution as a function of temperature. Open markers represent the average effective interdiffusion coefficient determined in Mg(Al) solid solution from each EPMA line scan, while the closed markers are those for the Mg(Zn) solid solution.
8. Al impurity diffusion coefficient in Mg as a function of temperature. Open markers represent the impurity diffusion coefficient determined from each EPMA line scan.
9. Zn impurity diffusion coefficient in Mg as a function of temperature. Open markers represent the impurity diffusion coefficient determined from each EPMA line scan.
10. Impurity diffusion coefficients of various solutes in Mg as a function of temperature.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10