Diffusion study of Mg-based alloys:

an experimental and modeling approach

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Abstract

Magnesium alloys are receiving global attention in transportation sectors thanks to their superior light weight capacity which allows the design of fuel efficient vehicles with lower CO₂ emissions. To develop commercial Mg alloys and optimize their manufacturing processes, fundamental knowledge in thermodynamics and diffusion kinetics is indispensable. This is particularly true for the production of wrought Mg alloys where several downstream processes such as solution treatment, rolling, extrusion, and annealing are required and where the products can be welded with other materials. In these thermally activated processes, diffusion can play a key role in the optimization of process parameters. A good knowledge of diffusion is thus imperative to understand the relationships between the microstructure and the high temperature process parameters. Unfortunately, there is a very limited number of studies on diffusion in Mg alloys. In the present study, diffusion kinetics of Mg alloys was investigated by both experiments and simulations.

Pure magnesium has an hcp crystal structure (c/a ratio = 1.6236, where c/a is the ratio of Mg lattice constants) and as a result, self-diffusion of Mg shows anisotropic behavior. Anisotropic diffusion is also observed for various alloying elements such as Ag, Cd, In, Sb, and Sn in hcp Mg. Apart from Ag, the diffusion of solute elements and Mg itself along the *a*-axis (the basal plane) of Mg is faster than along the *c*-axis (which is normal to the basal plane). However, the anisotropic behavior of the most common alloying elements like Al and Zn has not been investigated so far. Moreover, no data are available for rare earth elements (REE) despite the fact that their importance is increasing in Mg alloys.

In the present study, anisotropic diffusion behavior of Al, Zn, Gd, and Y were investigated using diffusion couple experiments with Mg single crystals. The anisotropic impurity diffusion coefficients of Al, Zn, Gd, and Y were found to follow the same trend as Mg-self diffusion and other alloying elements such as Cd, In, Sb, and Sn. Experimental data show that the diffusion coefficient along the basal plane is maximum and is about 1.3 times faster than along the

direction normal to the basal plane in the conventional material processing temperature. Moreover, the anisotropy in diffusion decreases with increasing temperature. In addition, the effect of the basal plane orientation of Mg on Al and Zn diffusion was investigated and it was found that the diffusion coefficients of Al and Zn in hcp Mg decrease linearly with an increase of the tilting angle of the basal plane. It is also found that the diffusion coefficients of Gd and Y are one order of magnitude lower than those of Al and Zn. Interdiffusion coefficients and growth constants of all binary intermetallics in Mg-Al, -Zn, -Gd, and -Y systems were also obtained from diffusion couple experiments.

The grain boundary diffusion of Al at high angle grain boundaries in polycrystalline Mg was also investigated with diffusion couple experiments. To obtain Al concentration profiles at the grain boundary, high resolution cold field emission-secondary electron microscope (CFE-SEM) energy dispersive spectroscopy (EDS), which can quantitatively analyze spot sizes of 10 nm, were used. Interestingly, the grain boundary diffusion of Al depends strongly on the misorientation angles between adjacent grains. Al diffusion at grain boundaries close to 75° misorientation is about two orders of magnitude higher than the one through for the bulk.

In the present study, diffusion simulation models were developed by numerical analysis of diffusion equations. A multiphase diffusion couple simulation model was developed which can successfully explain the experimental results. A homogenization and dissolution model was also developed to explain the solution treatment process of Mg-Al and Mg-Zn alloys. The model was validated with the help of annealing experiments for the binary Mg-Al (3, 6 and 9 wt. % Al) and Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) alloys. The model was then extended to the ternary Mg-Al-Zn system to predict the homogenization and dissolution phenomenon for the AZ series alloys.

The mutual solubilities of Mg and REE (Gd and Y) and the non-stoichiometries of intermetallics in the Mg-Gd and Mg-Y systems were also accurately determined with diffusion couple experiments. Based on our new phase diagram data and the data available in the literature, the thermodynamic modeling of the Mg-Gd and Mg-Y systems was performed.

Résumé

Les alliages de magnésium reçoivent une attention mondiale dans le secteur du transport grâce à leur faible poid qui permet la conception de véhicules économes en carburant qui réduisent les émissions de CO₂. Pour développer des alliages de Mg commerciaux et optimiser leurs processus de fabrication, une connaissance fondamentale de la thermodynamique et de la cinétique de diffusion est indispensable. Ceci est particulièrement vrai pour la production d'alliages de magnésium forgé où plusieurs processus tels que le traitement par solution, laminage, extrusion et recuit sont nécessaires et où les produits peuvent être soudés avec d'autres matériaux. Dans ces processus thermiquement activés, la diffusion peut jouer un rôle clé dans l'optimisation des paramètres du procédé. Il est donc impératif d'avoir une bonne connaissance de la diffusion pour comprendre les relations entre la microstructure et les paramètres de traitement à température élevée. Malheureusement, il y a un nombre très limité d'études sur la diffusion dans les alliages de magnésium. Dans la présente étude, la cinétique de diffusion dans les alliages de Mg a été étudiée par des expériences et des simulations.

Le magnésium pur a une structure cristalline hcp are un rapport c/a = 1,6236, (où c/a est le rapport des constantes du réseau de Mg) entrainant une l'autodiffusion est anisotrope dans sa structure. Une diffusion anisotrope est également observée pour différents éléments d'alliage tels que Ag, Cd, In, Sb, Sn et Mg dans le Mg hcp. A l'exception de Ag, la diffusion du Mg et des éléments de soluté le long de l'axe a (plan basal) est plus rapide que celle observée le long de l'axe c (qui est normal au plan de base) dans le Mg hcp. Toutefois, le comportement anisotrope des éléments d'alliage les plus courants tels que Al et Zn n'a pas été étudié jusqu'à présent. De plus, aucune donnée n'est disponible pour les éléments des terres rares (REE) en dépit du fait que leur importance augmente dans les alliages de magnésium.

Dans la présente étude, le comportement de diffusion anisotrope de Al, Zn, Gd et Y a été acquis à partir d'expériences avec des couples de diffusion sur des monocristaux de Mg. Les coefficients anisotropes de diffusion d'impuretés de Al, Zn, Gd et Y suivent la même tendance que pour l'autodiffusion du Mg et d'autres éléments d'alliage tels que Cd, In, Sb et Sn. Les données expérimentales montrent que le coefficient de diffusion le long du plan de base est maximum et est environ 1.3 fois plus rapide que celui le long de la direction normale au plan de base à la température normale de traitement du matériau. De plus, l'anisotropie de diffusion diminue lorsque la température augmente. En outre, l'effet de l'orientation du plan basal du Mg sur la diffusion de Al et Zn a été étudiée et on a constaté que les coefficients de diffusion de Al et Zn dans le Mg hcp diminue linéairement avec l'augmentation de l'angle de basculement du plan de base. Il est également constaté que les coefficients d'interdiffusion et les constantes de croissance de tous les intermétalliques binaires des systèmes Mg-Al, -Zn, -Gd et -Y ont également été obtenus à partir d'expériences de diffusion.

La diffusion aux joints des grains de Al à des angles élevés de joints dans du Mg polycristallin a également été étudiée à l'aide d'expériences de couple de diffusion. Pour obtenir des profils de concentration de Al aux joints de grain, la microscopie électronique à balayage dotée d'un canon à émission de champ froid (CFE-SEM) la spectroscopie à dispersion d'énergie (EDS), qui peut quantitativement analyser des points de 10 nm, ont été utilisés. La diffusion aux joints des grains de Al dépend fortement des angles de désorientation entre les grains adjacents. La diffusion aux joints des grains de Al à des angles de désorientation proches de 75° est d'environ deux ordres de grandeur plus élevé que celle estimée pour la diffusion globale.

Dans la présente étude, les modèles de simulation de diffusion ont été développées par analyse numérique des équations de diffusion. Un modèle de simulation de couple de diffusion multiphasique a été développé qui peut expliquer avec succès les résultats expérimentaux. Un modèle d'homogénéisation et de dissolution a également été développé pour expliquer le procédé de traitement par solution pour les alliages de Mg-Al et Mg-Zn. Le modèle a été validé à l'aide d'expériences de recuit pour les alliages binaires Mg-Al (3, 6 et 9 % poids d'Al) et Mg-Zn (1.5, 4.0 et 5.5 % poids de Zn). Le modèle a ensuite été étendu au système ternaire Mg-Al-Zn afin de prédire l'homogénéisation et le phénomène de dissolution des alliages de la série AZ.

Les solubilités mutuelles de Mg et des terres rares (Gd et Y) et la non stœchiométrie des intermétalliques dans les systèmes Mg-Gd et Mg-Y ont également été déterminés avec précision à l'aide d'expériences de couple de diffusion. Sur la base de nos nouvelles données de diagramme de phase et les données disponibles dans la littérature, la modélisation thermodynamique des systèmes Mg-Gd et Mg-Y a été réalisée.

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List of nomenclature

- δ : Kronecker delta
- μ : chemical potential
- Ω : mobility
- 5N: 99.999 percent pure or 5 normal
- c/a: lattice constant ratio for hexagonal closed pack Mg
- C: concentration
- D: diffusion coefficient
- D_o : diffusion prefactor
- D: interdiffusion coefficient
- D_{Mg}^{hcpMg} : Mg self-diffusion coefficient
- D_k^{hcpMg} : solute (k) diffusion coefficient in Mg
- $D_{\perp k}^{hcp-Mg}$: diffusion coefficient of solute k perpendicular to the c-axis of hcp Mg
- D_{II}^{hcp-Mg} : diffusion coefficient of solute k parallel to the c-axis of hcp Mg
- $D \perp / D_{\parallel}$: ratio of anisotropic diffusion coefficient in hcp Mg
- $\tilde{D_{k_j}^n}$: interdiffusion coefficient in multi-component system
- D_{eff} : effective diffusion coefficient

 D_{gb} : grain boundary diffusion coefficient

G: Gibbs free energy

 $g_{A^{\circ}}^{\circ}$ molar Gibbs energies of the pure A

 Δg_{AB} : Gibbs energy change for formation of two moles of (A-B) pairs

J: flux

 \tilde{J} : interdiffusion flux

k: growth constant

 k_o : growth constant prefactor

L: interaction parameter

M: number of particles diffusing per unit area

Q: activation energy

R: molar gas constant

 S^{config} : configurational entropy of mixing

T: absolute temperature

t: time

w: layer thickness of intermetallic phase

x: distance

 x_k : mole fraction of k

y: site fraction

List of abbreviations

1D: One Dimensional

BCC: Body Centre Cubic

BSE: Back Scattered Electron

CALPHAD: CALculation of PHAse Diagrams

CANMET: Canada Centre for Mineral and Energy Technology

CEF: Compound Energy Formalism

CFE-SEM: Cold Field Emission-Scanning Electron Microscope

EBSD: Electron Back Scattered Diffraction

ECCI: Electron Channeling Pattern Imaging

EDS: Electron Dispersive Spectroscopy

EPMA: Electron Probe Micro Analyzer

FCC: Face Centre Cubic

FDM: Finite Difference Method

FE-SEM: Field Emission-Scanning Electron Microscope

FNN: First-Nearest Neighbor

GB: Grain Boundary

GHG: Green House Gas

HCP: Hexagonal Close Packed

ICP: Inductive Coupled Plasma

IMC: Intermetallic

MQM: Modified Quasichemical Model

NMR: Nuclear Magnetic Resonance

NRF: National Research Foundation

NSERC: Natural Sciences and Engineering Research Council of Canada

ODF: Orientation Distribution Functions

OES: Optical Emission Spectroscopy

OM: Optical Microscopy

PPM: Parts Per Million

REE: Rare Earth Element

SE: Secondary Electron

SEM: Scanning Electron Microscope

USAMP: United States Automotive Materials Partnership

WDS: Wavelength Dispersive Spectroscopy

XRD: X-Ray Diffraction

ZFP: Zero Flux Plane

Chapter – 1

Introduction

1.1 General background

Increase in greenhouse gas (GHG) emission in modern civilization leads to global warming which is a very sensitive and pressing concern now-a-days. The major contribution in this GHG from human activity is carbon dioxide (CO_2), which covers 54.7% of the total GHG [1]. Since the beginning of the Industrial Revolution (taken as the year 1750), the burning of fossil fuels and extensive clearing of native forests has contributed to a 40% increase in the atmospheric concentration of CO₂, from 280 to 392 parts per million (ppm) in 2012 [2]. The principle contribution of CO₂ comes from burning the fossil fuels for road, rail, air and marine transportation. Many countries have started regulations and legislation towards reducing the emission of CO₂ to control the GHG; especially in the North America USA and Canada have taken initiative to reduce the emission of CO₂ in the transportation sector. The transportation sector covers 27.5% of the total source of GHG emission in USA [3] and they have a target to reduce 80% of their total GHG emission in the transportation sector by 2050 [4], whereas Canada targeted to reduce 45-65% by 2050 [5]. To achieve the projected target within the time frame, the main strategy would be making fuel efficient vehicles using lightweight materials within the vehicle engine and body. For instance, light weight vehicles increased the efficiency to 27.3 mile per gallon (mpg) in model year 2011, which saved 887 million gallons of fuel that reduced 8.3 million metric tons of CO₂ emission [5].

Magnesium, the lightest structural metal that is sixth most common element on earth, has attracted designers in aerospace and automotive industries due to its low density (1.74 g/cc), approximately 35% less dense than aluminum (2.70 g/cc) and 80% less dense than steel (7.86 g/cc). High specific strength and stiffness, excellent castability and machinability, absorption of vibration and good weldability also make magnesium a very competitive candidate in automotive applications [6, 7]. With 15% annual increase in the consumption of Mg alloys in the automobile

industries, the demand for a wider range of Mg alloys with lower thermal expansion, higher fatigue strength, higher creep strength and better corrosion resistance has also increased [8-10]

The application of automotive magnesium can be traced back to 1960's, but then magnesium was replaced by aluminum due to its high cost. Magnesium attracted the attention again in recent years because of the drive for fuel efficiency. Mg and their alloys find application in industrial sectors, such as desulfurization of steel, transportation, aerospace, structure, power tools, sporting goods, computer and electronics and more recently in biomedical applications [11]. Out of this wide spectrum of applications, the transportation sector consumes ~ 92 % of the total Mg produced in the world [12]. In fact, the growth and demand of lighter vehicles in transportation sector is mainly responsible for fuelling the worldwide interest in Mg and its alloys. Volkswagen used magnesium for the crankcase and transmission housing of the Beetle. These components weighed a total of 17 kg, which was said to represent a savings of 50 kg when compared with using cast iron components. This saving of weight played a critical role in improving the stability of the rear-engine vehicle [13]. Porsche first worked with a magnesium engine in 1928 [14]. Magnesium average usage and projected usage growth per car are given as 3 kg, 20 kg, and 50 kg for 2005, 2010 and 2015, respectively [15,16]. According to US Automotive Materials Partnership (USAMP) automotive industry will increase the use of Mg to 155 kg parts in vehicle replacing 290 kg of steel and aluminum parts by 2020. This weight reduction will reduce the fuel consumption which is about 2.0% of total transportation energy and will reduce the GHG emissions [17]. Motivation from these advantages of Mg and its alloys leads to a wide range of research opportunities; Canada has shown a very keen interest to utilize the promising potential of Mg and their alloys in developing a variety of application in automotive industries. Hence, one of the industrial partners General Motors Canada invested research funds for developing Mg and Mg based alloys for the transportation sector and current study is a part of this research project.

The greatest limitation for the usage of wrought magnesium is its poor formability at room temperature. Because of its hexagonal close packed (HCP) crystal structure, only two independent basal slip systems can be activated. However, the ductility of magnesium can be greatly improved at high temperature due to the activation of non-basal slip systems. With the

rapid increase in the demand for Mg alloys, the need for better understanding the influence of alloying elements on their mechanical, physical and thermodynamic properties, and furthermore the kinetics of materials transport in these alloys becomes inevitable. Moreover, mechanical and chemical properties of Mg alloys are especially sensitive to alloy composition which is controlled through the addition of various alloying agents that span much of the periodic table. So far many researchers have conduct their work by varying different alloying element and determine mechanical and structural properties. Some researchers also determined the thermodynamic properties of these magnesium alloys to optimize the composition and processing parameters.

Diffusion is a common phenomenon at higher temperature processes (e.g. heat treatment, rolling, casting, forging, etc.) and the creep mechanism at higher temperature is diffusion dependent for Mg and their alloys [18]. In general, the high temperature process requires through several trial and errors with assumptions and experience from similar materials to optimize the final products with desired physical and mechanical properties. This approach becomes inefficient, time consuming and expensive for most of cases. This is the reason people tend to adopt modeling approach instead of trial and error in modern age. A suitable diffusion model can be a useful tool to helpthe optimization of the process parameters (time and temperature). Commercial diffusion software like MultiDiflux [19, 20], Profiler [21-23], DICTRA [24], MatCalc [25] and VisiMat [26, 27] can simulate this high temperature processing steps in a virtual environment. Except VisiMat all others operate in DOS-based PC and VisiMat developed on Matlab code.

Use of this diffusion software is limited due to unknown steps that performed to generate concentration profiles for solute component in a multi-component system. As user has to input thermodynamic and kinetic data, user must have a good knowledge and reliable data bank to perform the calculations. There are good kinetic database for Fe-based and Ni-based alloys. Unfortunately there is no diffusion database for Mg based alloy, so it is difficult to perform diffusion simulation for Mg-based alloys.

1.2 Objectives

The main objective of this work is to understand the diffusion phenomenon for Mg alloys through both experimental and modeling approach and develop diffusion database simultaneously. To achieve this goal, anisotropic diffusion behavior of solute elements (Al, Zn, Y, and Gd) in Mg were determined using the diffusion couple experiments with Mg single crystals. Grain boundary diffusion which is common phenomenon in commercial alloys also investigated. The homogenization process of binary Mg-Al and Mg-Zn alloys were experimentally studied and a homogenization model incorporating second phase dissolution was developed using a numerical diffusion model with moving boundary to predict the microstructual evaluation during homogenization.

The contents of this thesis are organized as follows. In chapter 2, an overview of diffusion theory, the basic understanding of diffusion modeling is provided. In chapter 3, details of the experimental techniques and multiphase diffusion modeling steps are discussed for the current work. In chapters 4 and 5, anisotropic diffusion behavior of Al and Zn with impurity diffusion coefficient are presented from a multiphase diffusion model. In chapter 6, diffusion kinetics of Y and Gd are presented with correction of new phase boundary in Mg-Y and Mg-Gd phase diagrams. Chapter 7 contains effect of grain boundary diffusion in polycrystalline Mg is presented. In chapter 9, homogenization and dissolution model for Mg-Al, Mg-Zn, and Mg-Al-Zn is presented with Mg-Al and Mg-Zn experimental data. The overall summary of the present work and original contributions to knowledge are presented in chapter 10 and 11 respectively.

Finally, to achieve the targeted goal by 2020 for weight reduction of vehicles, Mg and its alloys are the prime choice for automotive industries. Most Mg alloys consists of a dilute solid solution with binary or ternary compounds because of the low solute solubilities in Mg. The ability to predict the solute behavior at high temperature processes will be very useful in optimizing process parameters of downstream processes for Mg alloys. In this work, a multiphase diffusion model with homogenization and dissolution model is developed along with a comprehensive diffusion

database for solute (Al, Zn, Gd, and Y) diffusion coefficient, which is a very important contribution to the diffusion kinetics community. The predictive capacity of the model was validated by conducting diffusion annealing experiments.

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Chapter – 2

Literature Review

This chapter focuses on the fundamentals of diffusion theories. The methodology to calculate the interdiffusion and impurity diffusion coefficient from diffusion couple experiment is explained. Literatures on the anisotropic diffusion study for hcp Mg and grain boundary diffusion are also reviewed. Finally, the chapter is concluded with the review of commercial diffusion simulation software such as DICTRA, MatCalc and VisiMat.

2.1 Diffusion

Diffusion is a kinetic process that leads to homogenization, or uniform mixing, of the chemical components in a phase by discrete jumps of atoms that always happens above absolute zero temperature. Diffusion in solids always occurs at atomic or molecular levels and with increasing time, the extent of homogenization increases. The length scale over which chemical homogeneity persists within a phase gradually extends to macroscopic distance. In thermodynamic term diffusion is a paradigm for positive entropy change which finishes by reaching thermodynamic equilibrium. In the most elementary diffusion processes, entropy is the only extensive variable which change during spontaneous thermal mixing, the volume, energy and total mole number remain constant [1]. Most of the high temperature materials processes are controlled by diffusion. These processes include but are not restricted to phase transformations, precipitation, homogenization, re-crystallization and grain growth. These processes affect the microstructure and properties of the material during processing and then in service. Hence, controlled progress or suppression of these processes is crucial in design of new materials as well as in determining the reliability of the materials in service. Since most of these processes are diffusion-controlled, the knowledge of diffusion behavior of various elements of the system becomes necessary in engineering new materials as well as modifying the properties of existing materials.

Over last two decades there has been an extensive development in the field of computational thermodynamics. By the application of CALPHAD (CALculation of PHAse Diagrams) approach. It enables the calculation of multi-component phase diagrams and the tracking of individual alloys during heat treatment or solidification by calculation of phase distributions and phase compositions. In the field of phase transformations it is a well-established procedure to estimate the rate of a phase transformation from the rate of volume diffusion of the different components and to assume that thermodynamic equilibrium is established locally at the moving phase interface [2]. However, if the thermodynamic behaviour and the volume diffusivities of a system are known then it is possible to estimate the migration rate of a phase interface without any experimental information on the phase transformation itself. Thus the approach has a strong predictive potential which should be of great practical importance in materials science.

As in the case of establishing the thermodynamic functions it is necessary to choose some model in which all the experimental information on diffusion can be analyzed. This will make convenient extrapolations and interpolations possible and will ensure a consistency check between different pieces of experimental information.

2.2 Diffusion mechanism

Depending on the diffusing species and matter transport phenomenon two common mechanisms for atomistic diffusion in crystalline solids are observed for volume diffusion. Volume diffusion is the terminology used to define diffusion into a grain which is different than the grain boundary diffusion.

2.2.1 Vacancy or substitution mechanism

Atoms can move from one lattice site to another if there is sufficient energy present for the atoms to overcome a local activation energy barrier with the presence of vacancies for the diffusing atoms to move into. The activation energy for a diffusing atom is the sum of the energy required to move the atom and also to move the vacancy.

In perfect crystals atoms would not move from one lattice site to another due to no free space around (all sites are occupied). In practice, there is no perfect crystal; crystalline solids have many point defects, dislocations etc. which are source of vacancies. An illustration of vacancy/substitution mechanism for diffusion of an atom A and the activation energy required to complete the migration process is shown in Fig. 2.1 (a). Diffusion process will complete when atom A will migrate from position 1 toward position 2 or the vacancy will move from position 2
towards position 1. Vacancy/substitution mechanism for diffusion takes place for pure crystalline solids and also for similar size of impurity atoms.



Fig. 2.1. (a) Illustration of vacancy/substitution mechanism for diffusion with energy barrier, (b) Illustration of interstitial mechanism for diffusion.

2.2.2 Interstitial mechanism

Crystalline solids have various interstitial sites depending on crystal structure. For instance, BCC (Body Centre Cubic) crystal will have more free space compared to FCC (Face Centre Cubic) crystal due to close pack structure and those interstitial sites makes it easier for small diffusing atoms like hydrogen, helium, carbon, nitrogen, etc. to squeeze through openings between interstitial sites and diffuse into a crystal. The activation energy for diffusion is the energy required for these atoms to squeeze through the interstitial sites between the host lattice atoms.

An illustration of interstitial mechanism for diffusion of small atoms within the interstitial sites of a crystal is presented in Fig. 2.1 (b). This mechanism usually takes place within foreign atoms and typically requires less activation energy compared to vacancy/substitution mechanism.

2.3 Types of diffusion

Depending on the diffusion mechanism and diffusing species several types of diffusion can happen in crystalline materials. The most common types of diffusions are: self-diffusion, impurity diffusion, and interdiffusion.

2.3.1 Self-diffusion

Self-diffusion is the spontaneous movement of an atom to a new lattice site in a crystal of its own species, especially in a crystalline solid the migration of constituent atoms or molecules within the bulk. The mechanism for self-diffusion is mainly vacancy/substitution. Concentration gradient is necessary for diffusion and for pure crystalline solid the concentration gradient is created by imposing radioactive tracer of the same solid. The tracer is chemically the same as the host solid (different isotope) so there is no chemical bond within the diffusing and host atoms. The self-diffusion is sometimes called tracer diffusion because of the use of radiotracer isotopes.

2.3.2 Impurity diffusion

Impurity diffusion involves impregnated foreign atoms in a crystalline solid which can be either substitution (vacancy) or interstitial mechanism. Impurity diffusion can be measured with radiotracer which is chemically different than host solid. The concentration of impurity is very low and is stable at solid solution (no chemical reaction). Impurity diffusion also termed as solute diffusion due to diffusion of solute in infinite dilution. Impurity diffusion has a wide range

of aspect for engineering applications. Different solute atoms usually undergo solid solution to strengthen alloys and improve their property. It is very important to have the knowledge of impurity diffusion to design high temperature processes for alloys.

2.3.3 Interdiffusion

Interdiffusion occurs in response to a concentration gradient or more rigorously for a gradient in chemical potential. Interdiffusion also rephrased as chemical diffusion due to presence of chemical gradient. Interdiffusion can be easily explained with diffusion couple, in typical case pure metal A is bonded to pure metal B and diffusion is permitted at high temperature.

Although both A and B atoms move, only one concentration profile is established. A single concentration profile is enough to describe the concentration profile changes in the couple and can be translated to other concentration profile. Schematic illustration of diffusion couple for pure A and B is shown in Fig. 2.2. At initial stage concentration of A in B region is zero and the same for B, but after heat is applied, due to the random atom movement intermixing of A and B results in A-B alloy formation and also A, B solid solutions. Diffusion of A and B occurs due to chemical composition gradient exists at the interface for both elements. Concentration profile of either A or B is enough to describe the entire concentration change in the couple.

The individual diffusion rates of A and B are usually different and hence, the partial or intrinsic diffusion coefficient of A and B can be determined from the diffusion couple with reference to the fluxes of A and B relative to the local lattice planes. The interdiffusion coefficient is actually the weighted average of the intrinsic diffusion coefficient of A and B.



Fig. 2.2. Schematic of diffusion couple for pure A and B metal: (a) initial stage, (b) after heat applied.

2.4 Diffusion equations

Although diffusion of atoms, or atomic migration, is always occurring in solids at temperatures above absolute zero, a gradient of concentration is required. In the presence of a concentration gradient $\partial C/\partial x$ (where *C* is the concentration and *x* is the distance) in one direction of a certain species of atom, a flux *J* (atoms/m²s, Kg/m²s) of atoms of the same species is established down the concentration gradient.



Fig. 2.3. Schematic illustration of concentration gradient and flux in a normal diffusion process.

Flux can be defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time (Fig. 2.3). Diffusional process can be either steady-state or non-steady-state. These two different types of diffusion processes are distinguished by use of flux, *J*. For steady-state diffusion flux is constant with time, whereas for non-steady-state diffusion, flux varies with time. A schematic view of concentration gradients with distance for both steady-state and non-steady-state diffusion processes are shown in Fig. 2.4.



Fig. 2.4. Schematic representations of steady-state and non-steady-state diffusion processes.

Fick [3] first proposed the phenomenological relation between the diffusion flux of a component and its concentration gradient for diffusion. Steady-state diffusion is described by Fick's first law which states that flux, *J*, is proportional to the concentration gradient. The constant of proportionality is called diffusion coefficient (diffusivity), D (m²/s). Diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs. Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. For the one-dimensional case, Fick's first law is given by:

$$J = -D\frac{\partial C}{\partial x} \tag{2.1}$$

The minus sign in the equation means that diffusion occurs down the concentration gradient. Although, the concentration gradient is often called the *driving force* for diffusion (but it is not a force in the mechanistic sense), it is more correct to consider the reduction in total free energy as the driving force. In most of the cases, the diffusion is measured in the laboratory fixed frame. Such diffusion is referred to as interdiffusion. The interdiffusion of an element due to its own concentration gradient and Fick's first law can be expressed in terms of interdiffusion coefficient.

$$\tilde{J}_{k}(x,t) = -\tilde{D}\frac{\partial C_{k}(x,t)}{\partial x}$$
(2.2)

Where, \tilde{J}_k is the interdiffusion flux of component k based on the laboratory fixed frame and $\frac{\partial C_k}{\partial x}$ is its concentration gradient at position x and time t. \tilde{D} is called the interdiffusion coefficient.

To produce a basis for measuring the diffusion coefficient, Eq. (2.2) is usually combined with the equation of continuity:

$$\left(\frac{\partial C_k}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_k}{\partial x}\right)_t$$
(2.3)

Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time. This is means that a type of atoms accumulates in a region or is depleted from a region (which may cause them to accumulate in another region). Eq. (2.3) tells us that the variation of concentration with respect to time at a position x is equal to the negative gradient of interdiffusion flux with respect to x at time t. Substituting Eq. (2.2) into Eq. (2.3) gives Fick's second law:

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_k}{\partial x} \right)$$
(2.4)

This equation is solved for different boundary conditions to derive expressions for concentration profiles. For cases in which D is independent of composition, or where the range of composition is small, Eq. (2.4) reduces as follows:

$$\frac{\partial C_k}{\partial t} = \tilde{D} \frac{\partial^2 C_k}{\partial x^2}$$
(2.5)

When \tilde{D} is a function of concentration *C*, then the differentiation of Eq. (2.4) yields Eq. (2.6)

$$\frac{\partial C_k}{\partial t} = \tilde{D} \frac{\partial^2 C_k}{\partial x^2} + \frac{\partial D}{\partial x} \frac{\partial C_k}{\partial x}$$
(2.6)

2.5 Factors influencing diffusion

The ease of a diffusion process is characterized by the parameter D, diffusivity. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

2.5.1 Diffusing species

If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the host matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Hence, size of diffusing species will have great influence on diffusivity of the system. Amount of vacancy or defects in host crystal is also very important for diffusion process, for instance, rate of diffusion is faster in polycrystalline host compared to single crystal. Magnitude of diffusion coefficient, *D* indicates the rate at which atoms will diffuse in host matrix.

2.5.2 Temperature

Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those needs to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature:

$$D = D_o \exp(-\frac{Q}{RT})$$

$$\ln D = \ln D_o - \frac{Q}{RT}$$
(2.7)

where D_o is a pre-exponential constant, Q is the activation energy for diffusion (J/mol, or eV/atom), R is molar gas constant (J/mol-K) and T is absolute temperature (K). From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between (*lnD*) and (*1/T*). Thus by plotting and considering the intercepts, values of Q and D_o can be found experimentally.



Fig. 2.5. Plot of logarithmic diffusion coefficient with reciprocal of absolute temperature for several common elements [4].

Some experimental diffusion coefficient values for common metals with temperature dependency are shown in Fig 2.5. Most of the engineering application is done between 773 and 1273 K (500 and 1000 °C) for metals. Diffusion is faster in lower meting materials.

2.5.3 Crystal structure and defects

Diffusion is faster in open lattices or in open directions than in closed directions. For instance, diffusion in BCC would be faster compared to FCC lattice. Presence of defects like dislocations,

grain boundaries act as short-circuit paths for diffusing species, where the activation energy is less. Thus the presence of defects enhances the diffusivity of diffusing species.

2.6. Binary diffusion

In a typical experimental diffusion couple assembled with two solid alloys, the diffusion zone is usually limited well within the ends of the two terminal alloys. For such a diffusion couple, called an infinite diffusion couple, the typical binary concentration profiles are schematically shown in Fig. 2.6. The terminal alloys, Alloy A and Alloy B, in Fig. 2.6 are characterized by the initial compositions (C_1^-, C_2^-) and (C_1^+, C_2^+) , respectively.



Fig. 2.6. Schematic concentration profiles of components 1 and 2 in a binary diffusion couple between Alloy A and Alloy B.



Distance, $x (\mu m)$

Fig. 2.7. Schematic Interdiffusion flux profile determined from the concentration profiles in Fig. 2.6.

Interdiffusion fluxes can be calculated at each position from this concentration versus distance curves from Eq. (2.2) and such flux profiles are shown in Fig. 2.7. It can be seen from Fig. 2.7 that the flux of component 1, J_1 is positive, whereas that for component 2, J_2 is negative throughout the diffusion zone. Thus, both the components diffuse down their own concentration gradients in opposite directions.

2.7. Multi-component diffusion

The detail description of multi-component diffusion was first proposed by Onsagar [5, 6] that served as the basis of both theoretical and experimental concept of diffusion studies in alloys with more than three components. Kirkaldy and Young have reviewed the major contributions
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and advances made on the area of multi-component diffusion throughout the last decade [1]. In an *n*-component system, there exist (n-1) independent concentrations. Onsager [5, 6] expressed the interdiffusion flux of a component *k* as a linear combination of (n-1) independent concentration gradients. This relation referred to as Onsager's formalism of Fick's law extended to multi-component system is expressed as follows:

$$\widetilde{J}_{k} = -\sum_{j=1}^{n-1} \widetilde{D}_{kj}^{n} \frac{\partial C_{j}}{\partial x}; \qquad k = 1,2 \qquad \dots \qquad (n-1)$$
(2.8)

where D_{kj}^n are called interdiffusion coefficients and the superscript *n* denotes that the component *n* is treated as a dependent component. Eq. (2.8) shows that to completely describe the interdiffusion in an *n*-component system, one needs the knowledge of $(n - 1)^2$ interdiffusion coefficients. The D_{kj}^n are called main interdiffusion coefficients when k = j and are called cross coefficients or interactive interdiffusion coefficients when $k \neq j$. The main coefficient is a measure of contribution to the interdiffusion flux of a component due to its own concentration gradient and the cross coefficients give the contributions to the flux due to the concentration gradients of other independent components. Thus, a cross coefficient characterizes the diffusional interaction between two components of a multi-component system.

The multi-component diffusion couples may exhibit maxima and/or minima along the concentration profiles of one or more components which never appear in binary diffusion couple. Schematic concentration profiles for three components of a ternary diffusion couple are shown in Fig. 2.8. The concentration profile for component 2 shows a maximum on the left side and a minimum on the right side of the couple in Fig. 2.8. Similarly, component 1 shows a minimum and a maximum on the left and the right sides, respectively. The reason for the maxima and /or minima in the concentration profile of component arises due to solute-solute interaction inside a multi-component alloy system. Such diffusion couples exhibiting extremes on the concentration

profiles of one or more components are characterized by uphill diffusion and/or Zero Flux Planes for the individual components [7, 8]. The diffusion of a component up its own concentration gradient is called uphill diffusion and the plane at which the interdiffusion flux of a component goes to zero within the diffusion zone is called Zero Flux Plane (ZFP).



Distance, $x (\mu m)$

Fig. 2.8. Schematic concentration profiles for a multi-component diffusion couple between two ternary alloys, Alloy C and Alloy D. The minima and maxima appearing on the concentration profiles of components 1 and 2 are typically observed for multi-component diffusion due to the diffusional interactions among various components.

2.8 Derivation of interdiffusion coefficient

As discussed earlier the interdiffusion of an element due to its own concentration gradient is quantitatively expressed in terms of its main interdiffusion coefficient. Most of the practically important materials are multi-component systems, meaning they consist of three or more elements. In multi-component systems, the interdiffusion behaviour of one component is affected by the presence of all other components of the system. Such diffusional interactions are quantitatively characterized in terms of interactive interdiffusion coefficients. Knowledge of the main and interactive interdiffusion coefficients is very important to predict the diffusion behaviour of multi-component systems. As discussed earlier an *n*-component system is characterized by (n-1) interdiffusion coefficients [5, 6], each of which is a function of composition of the system. This makes it very difficult to model the kinetics of multi-component systems and determining the interdiffusion coefficients as a function of composition becomes probably the most difficult step in modeling the kinetic behaviour of a multi-component system. A knowledge of interdiffusion coefficients is fruitless unless they can be used for the prediction of evolution of compositions in a given diffusion assembly and also assessed for their accuracy.

2.8.1 Kirkendall effect

When two alloys attached together (Fig. 2.6), a concentration gradient is established at the interface, which leads to diffusion of species and results in a concentration profile. The diffusion rate depends on many factors as discussed earlier results in dissimilar diffusion flux of species. The inequality of these fluxes leads to a net mass flow accompanying the interdiffusion process, which causes the diffusion couple to shrink on one side as to swell on the other side. This observation is first discovered by Kirkendall [9], and called Kirkendall effect after his name. The Kirkendall effect (shift) was observed by inserting inert wires (Mo, W, ThO₂ wires), at the initial interface. A schematic illustration of marker shift at the diffusion couple interface for A and B metal is shown in Fig. 2.9. The diffusion rate of metal B is faster compared to that of metal A which results in marker shifting towards metal B. Kirkendall proved this in copper-brass diffusion couple; Zn diffusion was faster compared to Cu resulting in shrinkage of brass which moved the Mo wires towards brass. So Kirkendall's effect is actually the shifting of a marker at the diffusion interface slightly in the opposite direction to the most rapidly moving species.



Fig. 2.9. Schematic illustration of marker shift at the diffusion couple interface.

2.8.2 Heumann-Matano method

The experimental approaches used to study the diffusion coefficient are (*i*) diffusion couple [10, 11], (*ii*) tracer sectioning [12-15], (*iii*) residual activity [16], (*iv*) analysis of grain boundary composition profile [17], and (*v*) nuclear magnetic resonance (NMR) [18]. Most of these techniques are used to determine tracer/impurity or self-diffusion in materials. However, the diffusion couple approach is the most common approach to determine the interdiffusion coefficient. One of the most well-known method of analyzing diffusion couple was proposed by Matano [19] in 1933 based on Fick's second law, originally proposed by Boltzman [20] in 1894. The diffusivity is assumed to be concentration dependent in this method. Matano-Boltzman method of determining the diffusivity *D* uses graphical integration. The first step is to plot the

concentration profile from diffusion couple end to end. The second step is to find the exact cross section where the total flux is equal on both sides (A and B), that plane is called Matano interface/plane (Fig. 2.10) and lies at the position where M and N are equal.



Fig. 2.10. C-x curve shows the Matano interface position where area M equals to area N.

The Matano interface is considered as the origin for the distance and the composition dependent interdiffusion coefficient at any point C can be determined by the Boltzman solution of Fick's law:

$$\tilde{D}(c) = -\frac{1}{2t} \frac{dx}{dc} \int_{0}^{c} x dc$$
(2.9)

where, $\int_{0}^{c} xdc$ is the total concentration under the curve from between 0 to *C*, *x* is the distance from the Matano interface (m), *t* is the diffusion time (sec), $\frac{dx}{dc}$ is the slope at point *C*. However, Matano-Boltzman method cannot be applied directly to the intermediate phases that formed during the diffusion couple experiment due to chemical inhomogeneity. Heumann [21] in 1952 derived an equation (Eq. (2.10)) for intermediate phases which is valid when the Page | 27 concentration of profile of the intermediate phase is linear throughout the phase from one end to the other end:

$$\tilde{D}_{k} = -\frac{1}{2t} \frac{w_{k}}{\Delta C_{k}} \int_{0}^{C_{k}^{1/2}} x dC_{k}$$
(2.10)

where D_k and C_k are the interdiffusion coefficient (m²/s) and the concentration of the solute of k phase, respectively, x the distance from the Matano interface (m), t the diffusion time (sec), w_k the layer thickness of k phase (m), ΔC_k the concentration difference of solute between the two ends of the k phase, and $C_k^{1/2}$ is the middle solute composition of the k phase.



Fig. 2.11. Schematic illustration of Heumann-Matano method [21].

An example of determining interdiffusion coefficient of intermediate phase using Heumann-Matano method is shown in Fig. 2.11. Interdiffusion coefficient of α phase can be determined by taking the hatched area in the figure for $\int_{0}^{C_{k}^{1/2}} x dC_{\alpha}$, ΔC_{α} is the difference between the end composition of α phase which is C_{3} - C_{2} , thickness is w_{α} and t is the diffusion time.

Relation between composition dependent diffusivities is illustrated in Fig. 2.12. Where, D is the interdiffusion, D_k is the intrinsic diffusion and D_k^* is the self-diffusion coefficient, respectively.



Fig. 2.12. Graphical representation of the composition dependence of the various diffusivities.

Relation between partial/intrinsic diffusion coefficients and interdiffusion coefficients can be described by Darken's equation [22]:

$$D = X_B D_A + X_A D_B \tag{2.11}$$

According to Eq. (2.11), interdiffusion coefficients at the two pure ends ($X_B = 0$ for pure A and $X_A = 0$ for pure B, where X_A and X_B are the mole fraction of A and B) are identical to the intrinsic diffusivities D_B or D_A , which at the pure ends are also the impurity diffusivities.

2.9 Diffusion study in Mg

Mg crystal has an anisotropic hcp crystal structure (c/a ratio = 1.6236, where c/a is the ratio of Mg lattice constants). Several researchers [23-25] performed experimental and modeling work on the self-diffusion in Mg and found anisotropy between the a-and c-axis diffusion. Shewmon [23] and Combronde [24] use Mg single crystal and perform radiotracer serial sectioning method, whereas Mantina [25] perform the first principle method for determining the self-diffusion in Mg. They all found the self-diffusion of Mg faster along the a-axis compared to that along the c-axis diffusion and the anisotropy were found between 1.13 to a maximum 1.26 within their experimental and calculation temperature ranges.

2.9.1 Anisotropic diffusion of solute in Mg

Various solute elements anisotropic diffusion in hcp Mg also reported in literature. Combronde [26] performed the experiments with Mg single crystal and radiotracer isotopes of impurity elements (Ag, Cd, In, Sb and Sn) and found anisotropic impurity diffusion coefficients. Except for Ag, all the impurity elements (Cd, In, Sb) in hcp Mg follow the same trend as the self-diffusion of Mg (Fig. 2.13). Impurity diffusion of Sn does not show much anisotropy whereas Ag shows an opposite trend to other impurity elements (Cd, In, Sb) in Mg.

Recently, Ganeshan [27] performed first principles calculations to estimate impurity diffusion coefficients of Al, Zn, Sn and Ca in dilute Mg alloy using an 8-frequency model within the local density approximation (LDA). They reported that except for Sn, all the impurity elements (Al, Zn, Ca) in hcp Mg follow the same trend as the self-diffusion of Mg. Impurity diffusion of Sn does not show much anisotropy whereas it shows an opposite trend to other impurity elements

(Cd, In, Sb) in Mg according to their calculation. All their calculated diffusion coefficients were about two orders of magnitude lower than the polycrystalline experimental values in literature.



Fig. 2.13. Anisotropic diffusion coefficients in hcp Mg [26].

Al and Zn are the most two common alloying elements in Mg, but no experimental data are available for the anisotropic diffusion behavior in hcp Mg. Diffusions of rear earth elements are also important for new generation Mg alloys, but unfortunately no systematic study of rare-earth diffusion in Mg alloys have been performed so far.

2.9.2 Solute diffusion and interdiffusion of intermetallics in Mg

Few researchers have also done some experiments with polycrystalline Mg to describe the solute diffusion coefficient and also interdiffusion of intermetallics for Mg/Al and Mg/Zn systems. Moreau [28] conducted diffusion couple studies using the junction between pure polycrystalline Mg and Mg-Al alloy (0 < Al < 20 wt. %) and determined the Al diffusion coefficient in hcp polycrystalline Mg between 623 and 693 K (350 and 420 °C). Funamizu [29] and Brubaker [30]

used the diffusion couple of Mg and Al to determine the interdiffusion coefficients and growth constant of β (Mg₁₇Al₁₂) and γ (Mg₂Al₃) phases between 638 and 698 K (365 and 425 °C). Recently, Brenann [31] conducted tracer diffusion experiments with Al in polycrystalline Mg to determine the Al diffusion coefficient in hcp polycrystalline Mg and they also performed diffusion couple experiments between 573 and 673 K (300 and 400 °C) to determine the interdiffusion coefficients of the β and γ phases [32].

Lal [33] measured the impurity (radiotracer serial sectioning) diffusion of Zn in polycrystalline Mg between 740 and 893 K (467 and 620 °C) using the radio tracer ⁶⁵Zn. On the other hand, Cermak [34] employed both radiotracer serial sectioning and residual activity to investigate the diffusion of Zn in polycrystalline Mg between 648 and 848 K (375 and 575 °C). Sakakura [35] also conducted a Mg-Zn diffusion couple experiment between 473 and 573 K (200 and 300 °C) and observed the intermediate compounds MgZn₂ and Mg₂Zn₁₁ at the interface of the diffusion couple. Using experimental data, they calculated growth constants and interdiffusion coefficients of Zn for the intermediate compounds. Very recently, Brennan et al. [36] also conducted Mg-Zn diffusion couple experiments between 568 and 598 K (295 and 325 °C), and reported four intermediate phases, Mg₅₁Zn₂₀, Mg₂Zn₃, MgZn₂ and Mg₂Zn₁₁, at the interface. They calculated the activation energies for growth constants of the MgZn₂ and Mg₂Zn₃ phases. Both diffusion couple studies were perform between polycrystalline Mg and Zn.

Lal [33] also reported diffusion of La and Ce in polycrystalline Mg between 813 and 868 K (540 and 595 °C) and 823 and 871 K (550 and 598 °C), respectively using diffusion couple technique. Recently, Zhao [37] and Bermudez [38] performed diffusion couple study between polycrystalline Mg and Y in the temperature range between 623 and 823 K (350 and 550°C). No diffusivity or mobility data were reported from their studies; their experimental data shows growth constants of $Mg_{24}Y_5$ and Mg_2Y phases only.

2.10 Grain boundary diffusion

Several types of crystal imperfection can exist to promote diffusion in polycrystalline materials. The most common imperfections are dislocation, excess vacancy and grain boundary.



Fig. 2.14. Comparison of diffusion coefficient in different region of Ag in Ag [39].

A grain boundary is actually accumulated dislocations which separates two regions of the same crystal structure in different orientation. Depending on the misorientation between two adjacent grains, grain boundaries are divided into small angle grain boundary (misorientation between adjacent grains is smaller than 15 $^{\circ}$) and high angle grain boundary (misorientation between adjacent grains is higher than 15 $^{\circ}$).

Because of the high amount of dislocation, grain boundary diffusion is much faster compared to bulk diffusion in lattice. With increasing misorientation the amount of dislocation increases between adjacent gains, which results in high diffusion through grain boundary. Turnbull [39] presented the difference of Ag diffusion in three different paths (Fig. 2.14). Grain boundary diffusion is much faster than volume diffusion due to les resistance structure of grain boundary. Off course, surface diffusion is even faster than grain boundary diffusion.

Harrison [40] described the influence of grain boundary on diffusion kinetics in solids and defines three distinct regimes for diffusion in polycrystalline material. A schematic of the three regimes is shown in Fig. 2.15, where *d* is the grain size, δ is the grain boundary width, *t* is the diffusion time, D_{eff} is the effective diffusion coefficient, *D* is the volume diffusion, D_{gb} is the grain boundary diffusion.



Fig. 2.15. Harrison's classification scheme for diffusion in polycrystalline solids [28].

The regime A is defined as overall diffusion where the diffusion length is larger than the grain size. Regime A can be usually found for long time diffusion at high temperature where the effective diffusion coefficient takes the role. The diffusion length for regime B in grains is noticeable but smaller than the grain size. Thus, diffusion occurs in grain boundary region with small contribution of grains. Diffusion length in regime C is negligible in grains and only happens at grain boundary region. Regime C can be achieved at very low temperature with short time annealing. Grain boundary diffusion can be properly investigated when the experimental samples are at regime B or regime C after diffusion annealing.

2.11 Commercial diffusion simulation software

2.11.1 DICTRA

DICTRA is most popular software to simulate homogenization and dissolution process of alloys which has developed by KTH and Thermocalc group in Sweden [41]. However, DICTRA software can only handle simple geometry such as planar, cylindrical, or spherical, of which can be reduced into one space variable. The accuracy of DICTRA simulation is highly dependent on the accuracy of the thermodynamic and mobility database. Thermodynamic and mobility database for steel is very well known and the diffusion calculations for Fe and Ni base alloys can be performed with DICTRA. No diffusivity or mobility data for Mg based alloys exists till now. The existing models in DICTRA are the single-phase model, the moving boundary model, the model for diffusion in dispersed system, the effective diffusion model, the cell model, the model for coarsening and the cooperative growth model. DICTRA doesn't have any multiphase diffusion model to extract the mobility or diffusivity value of solute in matrix which makes it difficult to simulate diffusion behavior for Mg based alloys.

2.11.2 MatCalc

MatCalc has been developed by a team of researchers at Vienna University of Technology, Austria [42], which mainly used for nucleation and precipitation kinetics of carbides and nitrides in steel. Like other diffusion software, MatCalc mobility database are focused on BCC and FCC metals (Fe, Al and Ni based alloys).

2.11.3 VisiMat

VisiMat is Matlab code with a graphical user interface developed at Purdue University [43, 44]. The diffusion calculations are done by constant diffusivity by square-root diffusivity method. Page | 35 VisiMat allows calculating diffusion in single-phase and multi-component diffusion couples. The program can accept user defined starting concentration profile and has the ability to visualize diffusion paths. As there is no thermodynamic database connected, the diffusion calculation for multiphase is not possible. Although the calculation is fast due to constant diffusivity, for each component the composition independent diffusion coefficients are typically valid only for dilute regions.

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Chapter – 3

Experiments and Modeling

In this chapter, various experimental techniques used in diffusion couple experiments and homogenization experiments for as-cast alloys are explicitly explained. The characterization and microanalysis techniques like Optical microscopy (OM), Scanning electron microscopy (SEM), Electron probe microanalyzer (EPMA) and XRD (x-ray diffraction) pole figure analysis are also discussed in this chapter. Finally, the multiphase diffusion simulation and homogenization simulation with moving boundary and flux balance equation are explained in brief.

3.1 Alloy Selection

The most common alloying elements for Mg are Al, Zn, Mn, Sn, Ca, Sr and REEs (Rare Earth Elements) to enhance mechanical and chemical properties of Mg. Among numerous alloys, AZ series alloys (Al and Zn are the two major alloying elements) are the most popular Mg alloys in automotive and aerospace applications. Al the most common alloying element for Mg is known for its good combination of improvement of room temperature strength, ductility and castability. Zn in Mg is well known to improve its strength by precipitation hardening. Mg based alloys with rear earth elements (REE) are drawing industrial attention due to the texture weakening effect of REE. Inspite of their importances, the anisotropic diffusion behaviors of Al, Zn, and REE in hcp Mg have not been studied so far. Hence the diffusion couple studies were carried out with Al, Zn, Y, and Gd for the present study to find their diffusion behavior in hcp Mg matrix. Homogenization experiments were carried out for Mg-Al (3, 6 and 9 wt. % Al), and Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) alloys to systematically investigate the homogenization process. The phase diagrams of the Mg-Al, Mg-Zn, Mg-Gd, and Mg-Y systems are shown in Fig. 3.1.









Fig 3.1. The binary phase diagrams of (a) Mg-Al, (b) Mg-Zn, (c) Mg-Gd, and (d) Mg-Y systems [1].

3.2 Diffusion couple experiment

Diffusion couple experiments were carried out between pure M metals (M = Al, Zn (Alfa Aesar), Y, and Gd (99.9 wt. %, HEFA Rare Earth Co. Ltd.)) and Mg (single crystal or polycrystalline Mg (99.99 wt. %, Magnesium Elektron)). Diffusion couple experiments were performed in following steps: production of Mg single crystal \rightarrow cutting of single crystals with proper direction \rightarrow diffusion couple assembling \rightarrow annealing of diffusion couple in controlled atmosphere \rightarrow water quenching \rightarrow characterization.

3.2.1 Production of Mg single crystal

Bridgman furnace method is the most widely used technique for manufacturing single crystal, developed by Bridgman in 1925 [2]. It is a relatively simple method that can control the size of single crystal and shape by using a crucible containing molten metal. This method can control the direction of growth using seed. Almost 40 percent of single crystals now-a-days are prepared by this method. However, growth of crystal may be stressed by contact with molten metal and the crucible. If solid-liquid interface doesn't keep stable, stray grains can be grown internally. This method is very widely used for industrial parts like turbine blade and bearing. The size of part manufactured by this method has no limit. But, flow control is very challenging for large parts. Maximum 300 mm diameter can be manufactured by this method without significant heat flow problem. Usually, single crystal of any material doesn't involve phase transformation between the melting point and room temperature while being grown by this method. The schematic diagram of typical vertical Bridgman furnace is illustrated in Fig. 3.2. There are many controlling factors such as material and size of the crucible, temperature profile in furnace, upper winding and lower winding oscillation rate of crucible, impurity in melting metal and the opening angle of the crucible. One has to find optimum conditions through many experiments and experiences to manufacture single crystal successfully. The steps for manufacturing is to put the feed metal into crucible and insert the crucible in furnace to melt completely above melting point and then solidify very slowly from one end to another end of the sample. Because the

crucible has contact with melting metal, the selection of crucible is very crucial. Most widely used crucible are conical shaped and are made of metal, ceramic or graphite.

The Mg single crystals used in the present study were produced by Prof. Tae Kwon Ha's research group in Gangneung-WonJu University, South Korea. A conical shaped graphite crucible was used to produce Mg single crystal without any crystal seed. Therefore, the basal plane direction of Mg cannot be controlled in the production.



Fig. 3.2. Sketch of a furnace for the vertical Bridgman method [2].

It took almost one day to produce one single crystal. The diameter of the cylindrical single crystal produced at Gangneung-WonJu University, South Korea was 10 mm and the length was between 100 to 150 mm.

3.2.2 Direction of Mg single crystal

Several characterization techniques were applied to confirm that the Mg bar produced from Bridgeman furnace is single crystal. All the Mg single crystals were checked under OM (Optical Microscope-Nikon equipped with Clemex vision system), followed by SEM (Hitachi Cold FE SU-8000) imaging and EBSD (Electron Back Scattered Diffraction). Single crystal orientation is very important for directional diffusion study and thus all the as received Mg single crystal bars were examined by XRD (Bruker D8) pole figure measurement to determine the basal plane of Mg bar. Unfortunately most cases, the basal plane of Mg single crystals was tilted towards different direction (Fig. 3.3) than the longitudinal direction of Mg bar.



Fig. 3.3. Illustration of XRD pole figure for {0001} plane of a Mg single crystal. The schematic diagram of the Mg bar shows the examination position by XRD.

To obtain the properly oriented Mg crystal sample, a special cutting jig was designed with a steel c-clamp and steel bar (Fig. 3.4). The cutting jig can rotate in both directions as shown in schematic to cut specimen at desired direction. All the single crystals were cut with the cutting

jig mount in a low speed diamond saw (Buehler IsoMet) in such direction so that the basal plane lies parallel to the flat surface of the cut Mg sample. To confirm orientation of Mg single crystal sample after cutting, XRD pole figure measurement was done on the flat surface of the sample. To obtain the pole figure, the Mg sample was oscillated in both X-Y direction 2 mm.



Fig. 3.4. Illustration of special cutting jig paired with the low speed saw and simplified schematic sketch of the cutting jig.

XRD pole figure for {0001} (the basal plane) plane from the flat surface is illustrated in Fig. 3.5. The pole figure shows that the basal plane is almost parallel to the surface of the single crystal. Each Mg single crystal sample was examined to make sure the basal plane lay parallel to the flat surface of the cylindrical specimen. These Mg single crystals were applied afterwards for the directional diffusion couple experiments with Al, Zn, Y, and Gd to investigate anisotropic diffusion behavior through the a- and c-axis of hcp Mg.


Fig. 3.5. Illustration of XRD pole figure for {0001} plane of a Mg single crystal after cutting. The schematic diagram shows the direction of XRD measurement for Mg sample cut.

3.2.3 Preparation of starting sample

The polycrystalline Al, Zn, Y, Gd, and Mg sample were sectioned into small pieces from ingot and ground to make half-circles of dimension 15 mm diameter and 10 mm thickness (Fig. 3.6). The specimens were annealed at 723 K (450 °C) under high purity Ar (5N) atmosphere to relieve any stress during the sample preparation and to obtain large grain size. The typical grain size obtained after annealing was larger than 1000 μ m. The polycrystalline Al, Zn, Gd, Y, and Mg samples were then polished with 0.25 μ m oil based diamond suspension (Buehler) in ethanol to obtain a flat surface to make proper contact for diffusion couple experiment.

The Mg single crystal was cut into small pieces which have either flat surface of the basal plane or perpendicular to the basal plane. The single crystal samples then ground very slowly and carefully to half-circle of dimension 15 mm diameter and 10 mm thickness. Single crystal also polished with 0.25 μ m oil based diamond suspension (Buehler) in ethanol to obtain a flat surface to make proper contact. The orientation of each Mg single crystal specimen was re-confirmed by an XRD pole figure measurement before the diffusion couple experiment.

3.2.4 Mounting, annealing, and quenching

The half-circle samples then mount in a circular steel clamp of diameter 15mm. Hand vice tool was used to attach both sample tightly into the clamp. Good contacts between surfaces are the most important step for diffusion to occur through the contact plane. Mg single crystals were attached with the Al, Zn, Y, and Gd half circular specimen. The contact surface of Mg single crystals was either parallel to the basal plane or perpendicular to the basal plane.

Metals such as Al, Zn, Y, Gd, and Mg are very susceptible to oxidation when expose to ambient atmosphere. Therefore, the diffusion couple experiments were carried out in a gas tight tube furnace filled with high purity Ar (5N) (Fig. 3.6). To minimize the oxidation of the sample, the diffusion couple sample was rapped with Ta foil and Ar (5N) gas was flowed at a rate of 10 ml/min during the entire annealing experiments. The temperature of the sample was measured using a K-type thermocouple just above the diffusion couple sample. The annealing experiments were performed within a wide span of time at various temperatures. Diffusion couples were taken out from the furnace and quickly quenched in ice cold water after designed annealing schedule. The mounted diffusion couple samples were cut exactly perpendicular to the diffusion contact plan using a low speed diamond saw and polished with 0.05 μ m OPS solution (colloidal silica suspension-Buehler). Illustration of diffusion couples before and after annealing was shown in Fig. 3.6.



(a)



Fig. 3.6. (a) Atmosphere controlled low temperature tube furnace with diffusion couple before and after, and (b) simplified schematic illustration of atmosphere controlled furnace.

3.3 Homogenization and dissolution experiment

Binary Mg-Al (3, 6, and 9 wt. % Al) and Mg-Zn (1.5, 4.0, and 5.5 wt. % Zn) alloys were brought from CANMET (Canada Centre for Mineral and Energy Technology), Ottawa for this study. The alloys were prepared by gravity casting in a water chill copper mould. The cooling rate during Page | 49 the casting measured by thermocouple was found to be 80 K per second. Samples from the top and sides were discarded to remove the irregular solidification at the surface. The ingots were cut into small rectangle. Each small rectangular specimen has a dimension 3.5cm x 1.4cm x 1cm. The specimens were then ground mechanically to remove sharp edges.

Two different temperatures 603 and 673 K (330 and 400 °C) were selected for annealing the binary alloys. The specimens were annealed for 1, 2, 4, and 8 hrs at each temperature. Annealing of the specimens was done in a box furnace (Carbolite RHF 1500). The temperature control of the furnace used was maintained within \pm 5 K. Schematic illustration of box furnace and position of the sample are shown in Fig. 3.7. The furnace was conditioned for 1 day before starting new homogenization experiment. Small rectangular samples were located in the box furnace chamber (Fig. 3.7) close to the thermocouple to measure the exact sample temperature. Samples were taken out from the furnace chamber and immediately quenched in ice cooled water to maintain the annealing solute profile.



Fig. 3.7. Box furnace with simplified schematic illustration and position of the sample.

There is always a chance to have deformed structure at the surface of specimen due to the experience of high strain rate while sectioning. Mg and its alloys are well known for plastic deformation during even cutting. There is a chance for the deformed surface to be re-crystallized during the heat treatment. Hence, to avoid confusion, each specimen was cut at the centre with diamond cutter (Buehler IsoMet) after annealing. Polishing was done for as cast and annealed specimen with sand papers (Buehler) from coarser to finer grids to obtain a flat surface. To remove all the scratches from the specimen surface, 3µm and 1µm size diamond suspensions were used with velvet polishing cloth at very low speed. Final polishing was done by 0.05 µm OPS solution. To remove residue solutions and dust that may adhere on the specimen surface, ultrasonic cleaning was carried out in ethanol for 20 minutes for each specimen and then dried with hot air.

3.4 Characterization of annealed samples

3.4.1 Optical microscopy

Optical microscopy was performed using a Nikon light optical microscope with a Clemex vision system. All the diffusion couple cross-sections after fine polishing and ultrasonic cleaning were checked under OM to observe the quality of intermetallic phase and only samples with good interface were considered for further characterization. Polycrystalline Mg-Al and Mg-Zn diffusion couple samples were etched with acetal-picral solution (4.2 g picric acid, 10ml H₂O, 10ml acetic acid and 70 ml ethanol) to measure the grain size of hcp Mg adjacent to the diffusion layer. The etching was performed by carefully immersing the samples in the etchant for 3 to 5 seconds and then cleaning the sample surface with running water and ethanol.

3.4.2 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed using a Philips XL-30 FE-SEM electron microscope for imaging. Back scattered electron (BSE) images were acquired at the interface to identify and measure different intermetallic layers. EDS (Electron Dispersive Spectroscopy)

spectrums were acquired at the interface to identify the nominal composition of intermetallic phase. Second phase fractions were measured from the BSE images of as cast and annealed binary Mg-Al (3, 6, and 9 wt. % Al) and Mg-Zn (1.5, 4.0, and 5.5 wt. % Zn) alloys using an image analysis with Image ^J software. The area analyzed for second phase fraction was chosen to be 3mm x 3mm for all samples in order to reduce statistical error. A Hitachi Cold FE SU-8000 SEM was used for microanalysis of solute elements in the hcp Mg solid solution region for Mg/Al diffusion couple. The microanalyses were performed at very low voltage to avoid contamination. An accelerating voltage of 5 kV was used with a 1.5 nA beam current, a spot size between 5 to 10 nm, and counting times of 5 seconds at each points. The microanalysis was performed by line scanning with a step size of $0.3 \mu m$. The quantitative Al concentration in the hcp Mg solid solution region was then extracted by a special technique developed at McGill [3]. Mg/Al polycrystalline diffusion couple cross-section was characterized by EBSD mapping at the interface to locate position of the grain boundary and also to determine the misorientation angle between adjacent Mg grains. Al concentrations through the grain boundary were then extracted by line scanning through the grain boundary with a step size of $0.3 \mu m$.

3.4.3 Electron probe microanalysis

The solute concentration profile at interface of each diffusion couple cross-section was measured using A JEOL 8900 Electron Probe Micro Analyzer (EPMA-JEOL 8900) equipped with wavelength dispersive spectroscopy (WDS) at McGill University. An accelerating voltage of 15 kV was used with a 20 nA beam current, a spot size between 0.5 to 1.0 µm, and counting times of 20 seconds on peaks and 20 seconds on background, detection limit was 0.05 wt. %. A step size of 2 µm was used during line scanning at interface for each case. Raw data were reduced with the PRZ corrections using pure Al, Zn, Gd, Y, and Mg in the solid solution regions; however, intermetallic compounds were used for the correction within the intermediate phases. Elemental composition mapping were acquired for Mg-Al and Mg-Zn polycrystalline diffusion couple cross-sections to locate the grain boundary (the solute concentration is higher at grain boundaries for faster diffusion through GB, Fig 3.8) in hcp Mg solid solution region and avoid those GB area while acquiring solute diffusion in bulk volume by line scanning.



Polycrystalline Mg Grain boundary Intermetallic phase

Fig. 3.8. Elemental composition map of the cross-section of Mg-Al polycrystalline diffusion couple.



Fig. 3.9. Schematic illustration of line scanning through grain boundary (both sided arrows in the diagram represent the directions of line scanning).

The microsegregration or chemical inhomegenity of solutes in the as cast and annealed Mg-Al (3, 6, and 9 wt. % Al) and Mg-Zn (1.5, 4.0, and 5.5 wt. % Zn) binary alloys were investigated using WDS. Secondary phases usually precipitate at the grain boundaries during solidification due to segregation. It is expected that these secondary phases dissolve with longer annealing time and higher annealing temperature. Again with increasing annealing time the solute have more time to diffuse throughout the matrix from the secondary phase due to the existing local concentration gradient at the grain boundary. Fig. 3.9 illustrates schematic of line scan technique for Mg-Al and Mg-Zn binary alloy before and after annealing.

Fig. 3.9 illustrates schematic microstructure of Mg-Al and Mg-Zn binary alloy before and after annealing. To make sure that the solute concentration throughout the whole sample through thickness is homogeneous, 9 different areas were chosen for as cast and annealed samples; 3 near the surface, three at quarter (3.5 mm from the surface) and three at the center region (7 mm from the surface). To investigate the change in concentration profile of solute at the grain boundary and matrix interface, line scan through grain boundary was done in 5 different grain boundaries for each specimen. The black lines in Fig. 3.9 show the line scan position. Secondary particles were very carefully avoided during line selection from the microstructure. EDS was done for randomly selected 10 particles for each specimen to make sure the particles composition. The overall solute concentration in the sample is almost constant throughout the thickness. This may be due to the higher cooling rate that exhibit during casting with copper mold.

3.4.4 XRD texture analysis

XRD pole figure measurement was performed in the present study for determining the basal plane direction within the Mg single crystal. The XRD texture analysis of the Mg single crystal samples (scanned area of each sample was 2 mm x 2 mm) was obtained using a Bruker Discover D8 equipped with HiSTAR area detector. The basal plane orientation for Mg-Al and Mg-Zn polycrystalline diffusion couple cross-section was measured for each big grain adjacent to the interface that contribute for the formation of intermetallic layer to explain the dependency of the basal plane orientation on solute diffusion coefficient.

3.5 Diffusion modeling

Prediction of solute concentration during high temperature processes (solution treatment, hot rolling, extrusion, annealing etc.) can be obtained by diffusion modeling to optimize the process parameters like time and temperature. Diffusion modeling is a very powerful tool to simulate nucleation, precipitation, dissolution and homogenization process in multi-component with multiphase system. The accuracy of diffusion simulation is highly dependent on the accuracy of the kinetic and thermodynamic data that been taken in to consideration. A series of thermodynamics and kinetics equations need to be solved to simulate the diffusion processes. In this study, the numerical solution of these equations was performed by finite difference method (FDM) and then coding was done in FORTRAN language. Thermodynamics (Gibbs free energy, interaction parameter, solubility limit) molar volume of each phase and kinetics (mobility and diffusivity) data can be collected from literature. Thermodynamic information was extracted from the Factsage FTlite database [1] and many kinetic parameters were determined in the present study by diffusion couple experiments.

3.5.1 Diffusion coefficient and mobility

The interdiffusion flux for solvent k, J_k , can be expressed as:

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^n \frac{\partial C_j}{\partial \mathbf{x}}$$
(3.1)

where diffusion coefficient D_{kj}^n can be expressed as a function of mole fraction, chemical potential and mobility of elements:

$$D_{kj}^{n} = \sum_{i} \left(\delta_{ik} - y_{k} \right) y_{i} \Omega_{i} \left(\frac{\partial \mu_{i}}{\partial y_{j}} - \frac{\partial \mu_{i}}{\partial y_{n}} \right)$$
(3.2)

where δ_{ik} is Kronecker delta, y is the mole fraction (originally site fraction, but if there are only substitutional elements y is the same as mole fraction), Ω is the mobility, μ is the chemical potential. The subscript *n* means solvent (Mg in this study) atom, *k* and *j* are substitutional solute atom, and *i* could be either solvent or substitutional solute atom. The notation for interdiffusion coefficient is conventionally \tilde{D} but in this chapter, *D* is used for simplification.

Diffusion coefficient for any Mg based binary alloy system can be deduced from Eq. (3.2) as:

$$D_M^{Mg} = y_M y_{Mg} \Omega_M \frac{d\mu_M}{dy_M} \quad \text{and} \quad D_{Mg}^{Mg} = y_M y_{Mg} \Omega_{Mg} \frac{d\mu_{Mg}}{dy_M}$$
(3.3)

where $y_{Mg} + y_M = 1$, and M is solute like Al, Zn, Gd and Y.

The main and interactive interdiffusion coefficients for Mg based ternary alloy system, for example Mg-Al-Zn system can be deduced from Eq. (3.2) as:

$$D_{AlAl} = (-y_{Al})(1 - y_{Al} - y_{Zn})(\Omega_{Mg})(\frac{d\mu_{Mg}}{dy_{Al}} - \frac{d\mu_{Mg}}{dy_{Mg}}) + (1 - y_{Al})(y_{Al})(\Omega_{Al})(\frac{d\mu_{Al}}{dy_{Al}} - \frac{d\mu_{Al}}{dy_{Mg}}) + (-y_{Al})(y_{Zn})(\Omega_{Zn})(\frac{d\mu_{Zn}}{dy_{Al}} - \frac{d\mu_{Zn}}{dy_{Mg}})$$
(3.4)

$$D_{ZnZn} = (-y_{Zn})(1 - y_{Al} - y_{Zn})(\Omega_{Mg})(\frac{d\mu_{Mg}}{dy_{Zn}} - \frac{d\mu_{Mg}}{dy_{Mg}}) + (-y_{Zn})(y_{Al})(\Omega_{Al})(\frac{d\mu_{Al}}{dy_{Zn}} - \frac{d\mu_{Al}}{dy_{Mg}}) + (1 - y_{Zn})(y_{Zn})(\Omega_{Zn})(\frac{d\mu_{Zn}}{dy_{Zn}} - \frac{d\mu_{Zn}}{dy_{Mg}})$$
(3.5)

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$$D_{AlZn} = (-y_{Al})(1 - y_{Al} - y_{Zn})(\Omega_{Mg})(\frac{d\mu_{Mg}}{dy_{Zn}} - \frac{d\mu_{Mg}}{dy_{Mg}}) + (1 - y_{Al})(y_{Al})(\Omega_{Al})(\frac{d\mu_{Al}}{dy_{Zn}} - \frac{d\mu_{Al}}{dy_{Mg}}) + (-y_{Al})(y_{Zn})(\Omega_{Zn})(\frac{d\mu_{Zn}}{dy_{Zn}} - \frac{d\mu_{Zn}}{dy_{Mg}})$$
(3.6)

$$D_{ZnAl} = (-y_{Zn})(1 - y_{Al} - y_{Zn})(\Omega_{Mg})(\frac{d\mu_{Mg}}{dy_{Al}} - \frac{d\mu_{Mg}}{dy_{Mg}}) + (-y_{Zn})(y_{Al})(\Omega_{Al})(\frac{d\mu_{Al}}{dy_{Al}} - \frac{d\mu_{Al}}{dy_{Mg}}) + (1 - y_{Zn})(y_{Zn})(\Omega_{Zn})(\frac{d\mu_{Zn}}{dy_{Al}} - \frac{d\mu_{Zn}}{dy_{Mg}})$$
(3.7)

where $y_{Mg} + y_{Al} + y_{Zn} = 1$.

In the present study, the diffusion calculations were performed up to ternary system. Of course, if necessary, the diffusion coefficients can be extracted to higher order system using Eq. (3.2).

3.5.2 Numerical analysis

The basic assumptions that were taken into account in the present diffusion modeling are:

- a. One dimensional (1D) space.
- b. The composition of each phase at the phase interface is constant.
- c. The phase interface is always at equilibrium state.

The algorithm for diffusion simulation code is shown as simple flowchart (Fig. 3.10). As discussed earlier the diffusion phenomenon of a component in each phase can be described by Fick's second law:

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x} \left(D_k \frac{\partial C_k}{\partial x} \right)$$
(3.8)

As shown before when D_k is independent of composition, Eq. (3.1) can be written as follows:

$$\frac{\partial C_k}{\partial t} = D_k \frac{\partial^2 C_k}{\partial x^2}$$
(3.9)

When D_k is a function of composition C_k , then diffusion equation can be expressed as:

$$\frac{\partial C_k}{\partial t} = D_k \frac{\partial^2 C_k}{\partial x^2} + \frac{\partial D_k}{\partial x} \frac{\partial C_k}{\partial x}$$
(3.10)

Eq. (3.10) is used for diffusion modeling to simulate solute concentration profile.



Fig. 3.10. Algorithm for diffusion simulation in multiphase system.

when C_k is a function of time and space, then diffusion equation (Fick's second law) can be expressed in a generalized form:

$$\frac{\partial C_{k(x,t)}}{\partial t} = \frac{D_k}{x^a} \frac{\partial}{\partial x} \left(x^a \frac{\partial C_{k(x,t)}}{\partial x} \right)$$
(3.11)

Eq. (3.11) can be used to deduce the diffusion equation in planar, cylindrical and spherical coordinate assumption. When superscript 'a' is zero Eq. (3.11) reduced to Eq. (3.9) which is planar geometry, Eq. (3.11) becomes cylindrical geometry with a = 1:

$$\frac{\partial C_k}{\partial t} = D_k \left(\frac{\partial^2 C_k}{\partial x^2} + \frac{1}{x} \frac{\partial C_k}{\partial x} \right)$$
(3.12)

Eq (3.11) can be deduced to spherical coordinates for a = 2:

$$\frac{\partial C_k}{\partial t} = D_k \left(\frac{\partial^2 C_k}{\partial x^2} + \frac{2}{x} \frac{\partial C_k}{\partial x} \right)$$
(3.13)

For the present diffusion simulation solid solution region and intermetallics were considered as planar except $Mg_{17}Al_{12}$ was assumed to be cylindrical. $Mg_{17}Al_{12}$ phase was assumed as planar, cylindrical and spherical symmetry while carrying out the calculation multiphase diffusion simulation and cylindrical symmetry gives the most accurate fit with experimental data. According to the simulation, the change in geometric symmetry did not significantly change the result. Hence all the other intermetallics were considered as planar in the present diffusion simulation. Numerical analysis of the equation was done using the explicit FDM. Central difference approximation was used for space, whereas the forward difference approximation was used for space, whereas the forward difference approximation was used for space.

$$\frac{\partial C}{\partial t} = \frac{C_i^{j+1} - C_i^{j}}{\Delta t}$$
(3.14)

$$\frac{\partial}{\partial x} \left[D_i \frac{\partial C_i}{\partial x} \right] = \frac{1}{\Delta x} \left[\frac{D_{i+1} + D_i}{2} \frac{C_{i+1}^j - C_i^j}{\Delta x} - \frac{D_i + D_{i-1}}{2} \frac{C_i^j - C_{i-1}^j}{\Delta x} \right]$$
(3.15)

where *i* is space grid number and *j* is time-step number, Δt is time-step interval and Δx is grid spacing. The figure below (Fig. 3.11) shows a schematic representation of space grid and time space, from where the forward and central approach can be understood along with grid spacing.

Substituting Eq. (3.14) and Eq. (3.15) in Eq. (3.10) the solution of the diffusion equation can be deduced as follows:

$$C_i^{j+1} = C_i^j + \frac{\Delta t}{2(\Delta x)^2} [(D_{i+1} + D_i)(C_{i+1}^j - C_i^j) - (D_i + D_{i-1})(C_i^j - C_{i-1}^j)]$$
(3.16)



Fig. 3.11. Schematic representation of space grid and time step.

Eq. (3.16) is the numerical solution for the diffusion equation. FDM approximation has some error and to minimize error sometimes mixed approximation is used. Hence, both central and forward approximation is used to solve the diffusion equation. For the stability of FDM approximation Δt must be chosen with respect to the constant present in that equation. Time step Δt is chosen according to Eq. (3.17) for the stability of the FDM solution:

$$2D_k \frac{\Delta t}{\left(\Delta x\right)^2} \le 1 \tag{3.17}$$

3.5.3 Multiphase diffusion simulation

In multiphase diffusion the most critical part is the moving boundary problem (also known as Stefan problem) at interface. To simulate multiphase diffusion, the moving boundary problem must be solved. Different ways have been treated by many researchers to control this moving boundary problem [3-7]. Some researcher used a flexible-grid scheme (variable space network) in which the total grid expands to match the interface motion. When the grid expands, the concentrations at each gird must be adjusted. The most common method of shifting the grid positions and adjusting the grid concentrations is that referred to as a "Murray-Landis" transformation [5]. This transformation expands/shrinks the grids an amount proportional to their position from the moving boundary to maintain uniform grid spacing. The Murray-Landis transformation can be treated by either implicit or explicit finite difference methods. Many researchers have applied the Murray-Landis transformation [8-11]. Another scheme is a fixed grid scheme [4].



Fig. 3.12. Schematic diagram of initial condition for diffusion couple.

Fig. 3.12 showing the initial state (t = 0) of the simulation that consists of HCP Mg at the left side and solute metal at the right side for multiphase diffusion couple simulation. In the simulation, it is assumed that the nucleation time of intermetallic phases is negligible compared to the annealing time. As the nucleation is not part of this code, very thin (0.1 μ m) of intermetallic layer were already added in the simulation at t = 0. The final state of different phases that exists after time t >0 is shown in Fig. 3.13. After annealing the different intermetallics formed at the interface start to grow with annealing time to thicken the layers. Fig. 3.13 also defines the grid system that used for the multiphase diffusion simulation.



Fig. 3.13. Schematic concentration profile of binary diffusion couple after annealing at higher temperature.

In the present study, the moving boundary problem was solved by Murray-Landis transformation method [5]. It involves the transformation of the concentration-distance profile to allow for the movement to the phase interfaces. Simulation steps followed by the substantial derivative for the i_{th} grid:

$$\frac{dC_k}{dt} = \frac{\partial C_k}{\partial x} \left(\frac{dx}{dt}\right) + \frac{\partial C_k}{\partial t}$$
(3.18)

where *n* is total number of grid at each phase, $\left(\frac{dx}{dt}\right)$ is the velocity at the interface for each phase. The velocity at the interface is calculated based on the flux balance equation:

$$\frac{dx}{dt} = \frac{J_k^{R/L} - J_k^{L/R}}{C_k^{R/L} - C_k^{L/R}}$$
(3.19)

where x is the location of the interface and $J_k^{R/L}$, $J_k^{L/R}$ and $C_k^{R/L}$, $C_k^{L/R}$ are fluxes and concentration of component k at at the interface for each phase, respectively. Partial up winding was performed to remove the oscillation at the interface that may be arising due to large change in concentration gradient at the interface. The boundary conditions at the left interface of phase 1(hcp Mg) and right interface of phase 4 (solute) are based on zero mass transfer assumption:

$$C_{1,phase1} = C_{3,phase1} \tag{3.20}$$

$$C_{n_4+1, phase4} = C_{n_4-1, phase4} \tag{3.21}$$

It means that concentration gradient is regarded as zero at the both boundary (zero mass transfer).

Considering all the above assumptions, the diffusion program was written in FORTRAN language with explicit FDM formulation of diffusion equations. The program was written to predict the concentration profile and the boundary movement at the interface between Mg and solute metal with the growth of intermetallic layers. The initial compositions of Mg in the left side and solute metal in the right side are taken as 99.99. The interface composition of each phase is given as input in the simulation from the optimized Mg-X (Al, Zn, Gd, and Y) binary phase diagram (Fig. 3.1). The chemical potential of Mg and solute metal is hcp solution is calculated from the optimized thermodynamic model in Factsage FTlite database [1], which are also given as inputs in the program. Initially the thickness of intermetallic phases is considered as 0.1 µm. Mobility and thermodynamic data for each phase are given into the program as inputs.

The program begins with asking the annealing temperature and the annealing time at which the user wants to predict the solute concentration profile with new interface position and intermetallic thickness. The program gives output in a text file which can be easily imported into Microsoft ExcelTM program to see the predicted concentration profile.

3.5.4 Homogenization simulation

Homogenization simulation code for as-cast microstructure of Mg alloy was also developed. Considering as-cast microstructure, two sub-simulations are performed in this code: (*i*) dissolution of second phase in grain boundary and (*ii*) homogenization of microsegregation (solute) in grain. For dissolution of second phase, moving boundary was considered between the Mg solid solution grain and second phase at grain boundary. Amount of second phase was given as an input in length scale from the as cast microstructure. The concentration gradient is assumed as zero at the both boundary (zero mass transfer). For the homogenization of microsegregation in grain, concentration profile of solute between the cores of two adjacent grains is entered as input. The simulation is performed in single phase hcp solid solution without any moving boundary. Zero mass transfer is assumed at both sides. The general input data for thermodynamic and mobility are the same as the multiphase diffusion simulation.

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Chapter – 4

Anisotropic diffusion behavior of Al in Mg: Diffusion couple study using Mg single crystal

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Dr. Y. M. Kim assisted as a post-doctoral fellow in developing the multiphase diffusion program. Prof. T. K. Ha produced the Mg single crystals necessary for the experimental study. Prof. R. Gauvin provided with a new technique for quantitative analysis of Al with CFE-SEM. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision. All the Co-Authors provided valuable suggestions and comments and reviewed the manuscript before submission.

4.1 Abstract

The anisotropic diffusion behavior of Al in hcp Mg was for the first time experimentally investigated using the diffusion couple technique with single crystal Mg at the temperature between 638 and 693 K (365 and 420 °C). The diffusion coefficients derived from Al profiles in single crystal hcp Mg are: $D_{\perp Al}^{hcp-Mg} = 4.86 \times 10^{-3} (\text{m}^2/\text{s}) \exp(-154484/\text{RT})$ and $D_{II Al}^{hcp-Mg} = 9.51 \times 10^{-3} \exp(-159476/\text{RT})$. The diffusion coefficient of Al within basal plane is about 1.3 times higher than that along normal direction of basal plane at the experimental temperatures. The interdiffusion coefficients of Mg₁₇Al₁₂ and Mg₂Al₃ solid solutions were also derived and the values are similar to the previous studies.

Keywords: magnesium alloys, anisotropic diffusion, aluminum, diffusion couple, single crystal.

4.2. Introduction

Mg is one of the most promising metals for weight reduction in the transportation sector. Mg is typically alloyed with Al, Zn, Mn, Sn, Ca, Sr and REEs (Rare Earth Elements) to enhance its mechanical and chemical properties. In order to understand and predict the complex chemical reactions, both thermodynamic and kinetic knowledge of Mg alloys are indispensible. Although many thermodynamic studies including phase diagram determination and thermodynamic modeling were recently carried out, the diffusion of alloying elements in Mg is not very well investigated yet. In particular, the diffusion in Mg alloys can be important to understand the creep behavior, to design the heat treatment process, and to predict the precipitation behavior of secondary phases.

Mg has the hcp crystal structure (c/a ratio = 1.6236). Therefore, the diffusion of alloying element in hcp Mg phase should be anisotropic, which makes diffusion studies more difficult. Shewmon [1] and Combronde et al. [2] investigated the self-diffusion coefficients of Mg using a radiotracer serial sectioning method. They used Mg single crystals in their experiments and concluded that the self-diffusion coefficient of Mg perpendicular to the c-axis is higher than that along the caxis. Mantina [3] calculated the self-diffusion coefficients for Mg using first principles calculations and reached the same conclusion. Unfortunately, there is no experimental study for the anisotropic diffusion behavior, even for Al, the major alloying element of Mg alloys.

Although Al diffusion in Mg was previously investigated, all the experiments were performed using polycrystalline Mg so that the anisotropic diffusion of Al was not measured properly. For example, Moreau et al. [4] conducted diffusion couple studies using the junction between pure polycrystalline Mg and Mg-Al alloy (0 < Al < 20 wt. %) and determined the Al diffusion coefficient in hcp polycrystalline Mg between 623 and 693 K (350 and 420 °C). Funamizu et al. [5] and Brubaker et al. [6] used the diffusion couple of Mg and Al to determine the interdiffusion coefficients and growth constant of β (Mg₁₇Al₁₂) and γ (Mg₂Al₃) phases between 638 and 698 K Page | 69 (365 and 425 °C). Recently, Brenann et al. [7] conducted tracer diffusion experiments with Al in polycrystalline Mg to determine the Al diffusion coefficient in hcp polycrystalline Mg and they also performed diffusion couple experiments between 573 and 673 K (300 and 400 °C) to determine the interdiffusion coefficients of the β and γ phases [8]. Very recently, Ganeshan et al. [9] performed first principles calculations for impurity diffusion coefficients in dilute Mg alloy for Al, Zn, Sn and Ca using their 8-fequency model. They report that the directional diffusion coefficient of Al in hcp Mg along the a-axis is $1.2 \sim 3.2$ times higher than that along the c-axis between 400 and 1000 K (127 and 727 °C), but the calculated values for diffusion coefficients were about 2 orders of magnitude lower than the polycrystalline experimental value of Brenann et al. [7].

No experiments for the anisotropic diffusion behavior of Al in hcp Mg have been performed using Mg single crystals. In the present study, the anisotropic diffusion behavior of Al in Mg was experimentally studied using the diffusion couple with Mg single crystal to investigate the difference of Al diffusion along the a- and c-axis of hcp Mg crystal. In addition, the interdiffusion and growth constants of intermetallic phases in the Mg-Al system were examined.

4.3. Experimental

Magnesium single crystals were produced using a modified Bridgman furnace located at Gangneung-WonJu University, Korea. In order to prevent oxidation the Mg bars were machined from high purity Mg ingots (99.99%, Magnesium Elektron) and inserted to a cylinder-shaped mould made of graphite. Each solidified Mg sample was characterized as a single crystal using Electron Backscattered Diffraction (EBSD) and X-Ray Diffraction (XRD). Unfortunately, the direction of each Mg single crystal was not controlled because no pre-single crystal seed was used in the experiment. Instead, the solidification was designed to begin at the tip of the graphite cylinder to a produce cylindrical single crystal of maximum length of 15 cm and 10 mm in diameter. All the specimens produced in the Bridgman furnace were examined to check the Page | 70

direction of the single crystals using a Bruker D8 XRD pole figure measurement. Each single crystal was cut very carefully using a Buehler IsoMet diamond saw with a specially designed cutting jig to obtain sample crystals with the surface parallel/perpendicular to the basal plane of the Mg structure. In order to avoid surface deformation, very low speed was used for cutting. Polycrystalline pure Al (99.99%, Alfa Aesar) was sectioned into a bar with 15 mm in diameter and 10 mm in thickness from a large ingot. After cutting the bars into half-circular disc using a low speed saw, Al specimens were annealed at 723 K (450 °C) under high purity Ar atmosphere to relieve any stress during the sample preparation and obtain a large grain size. The grain size of Al was larger than 1000 µm. Then, the Mg and Al specimens were polished down to 0.25 µm with oil based diamond suspension (Buehler) with ethanol to obtain a flat surface. The orientation of each Mg single crystal specimen was re-confirmed by an XRD pole figure measurement before the diffusion experiment. Discs made of Mg and Al were tied with a stainless steel clamp well enough to make sure that the surfaces of the specimens were in perfect contact with each other. Mg single crystals were attached with polycrystalline Al on the basal (0001) plane so that Al will diffuse along the c-axis and Mg single crystals were also attached with polycrystalline Al perpendicular to the basal (0001) plane to make sure Al will diffuse along a-axis.

Diffusion couple experiments were carried out in a gas tight tube furnace. In order to minimize the oxidation of the sample, the diffusion couple samples were wrapped with Ta foil and high purity Ar gas (5 N) was flowed at 10 ml/min during each experiment. The temperature of the specimen was measured using K-type thermocouple just above the diffusion couple sample. The annealing experiments were done at 638, 663, 673 and 693 K (365, 390, 400 and 420 °C) for 48, 72 and 94 hrs to make sure that all intermetallic phases developed enough layers in the solid state. After the annealing, specimens were taken out from the furnace and quickly quenched in water. The mounted diffusion couple samples were cut exactly perpendicular to the diffusion contact plane using a diamond saw with low speed and polished with 0.05 µm colloidal silica suspension. Each diffusion couple were examine under optical microscope to make sure the intermetallic layers are perfect and then only for the good samples; intermetallic phases, Mg and Al solid solutions were examined using both Hitachi SU-8000 Field Emission-Scanning Electron

Microscope (FE-SEM) and JEOL 8900 Electron Probe Micro Analyzer (EPMA). In particular, the Al concentration profiles through the interface and inside the hcp Mg were measured by EPMA- Wavelength Dispersive Spectroscopy (WDS) with 15 keV and FE-SEM- Energy Dispersive Spectroscopy (EDS) with 5 keV. The Al concentration was determined in the FE-SEM with a new ratio method that is described in detail by Gauvin et al. [10].

4.4. Results and discussion

Fig. 4.1 shows the back scattered SEM image of the diffusion couple sample annealed at 693 K (420 °C) for 72 hrs. The Al concentration profile determined with EPMA-WDS and the typical XRD pole figures of single crystal Mg perpendicular and horizontal to basal plane (0001) of Mg are also presented in the figure. Backscattered SEM image for the sample confirmed the existence of two intermetallic phases (γ -Mg₁₇Al₁₂ and β -Mg₂Al₃ solid solutions) at 663, 673 and 693 K (390, 400 and 420 °C). In the case of the samples annealed at 638 K (365 °C), small discontinuous Mg₂₃Al₃₀ phase was observed between Mg₁₇Al₁₂ and Mg₂Al₃ phases. Presence of Kirkendall effect [11] was observed by optical microscope and also confirmed by WDS. Based on the EPMA-WDS line scan, the exact interfaces between hcp Mg, intermetallic phases and fcc Al were determined and the composition variations in the intermetallic phases were accurately determined. The distances of the intermetallic layers from original Mg/Al interface marked in the samples were measured to find the interdiffusion coefficient. Most of intermetallic phases formed toward Mg side because the diffusion of Al in hcp Mg is faster than that of Mg in fcc Al. The experimental results are summarized in Table 4.1.

Theoretically MgO or Al_2O_3 can be easily formed at the surface of Mg and Al, respectively during the sample preparation and annealing. In order to prevent this as much as possible, we took a special care in the sample preparation (using oil-based diamond suspension with ethanol) and annealing (wrapping with Ta foil and high purity Ar atmosphere). As a result, there was almost no oxide layer formed at the original interface (Matano interface). Only some small and Page | 72 discontinuous oxide particles were observed at the interface, which would merely influence to the diffusion behavior in the present study.

4.4.1. Growth constants and interdiffusion coefficients of intermetallic phases

Growth constants for both $Mg_{17}Al_{12}$ and Mg_2Al_3 phases were determined to find the growth kinetics for the intermediate phases. A parabolic growth constant based on diffusion-controlled growth can be assumed:

$$x = k\sqrt{t} \tag{4.1}$$

where x is the thickness of intermetallic phase, t is annealing time and k is growth constant of which temperature dependency can be expressed by the following Arrhenius relationship:

$$k = k_0 \exp(-Q/RT) \tag{4.2}$$

where k_o (m/s^{0.5}) is the pre-exponential factor, R (J/mol-K) the gas constant, Q (J) the activation energy and T the annealing temperature in Kelvin.

The Eq. (4.1) assumes that the nucleation time of the intermetallic phases can be negligible in comparison with the present annealing time. In order to prove this is valid assumption, the layer thickness of intermetallic phases is plotted against the square root of time in Fig. 4.2. As can be seen in the figure, the linear extrapolation of the experimental points can reach to origin, which proves that the nucleation time is negligible compared with the annealing time. Therefore, the

calculations of the growth constant and diffusivity of intermetallic phases and diffusivity of Al in Mg phase from present study are accurate.

The calculated growth constants and activation energies of both $Mg_{17}Al_{12}$ and Mg_2Al_3 phases are listed in Table 4.2 in comparison with the previous studies [5, 6 and 8] and also shown in Fig. 4.3. The activation energies for the $Mg_{17}Al_{12}$ phase from our study are in good agreement with the results of Brenann et al. [8] and Funamizu et al. [5], whereas our activation energy for Mg_2Al_3 phase are in good agreement with the results of Funamizu et al. [5]. The activation energies of Brubaker et al. [6] are much higher than the present results.

The interdiffusion coefficient of intermetallic phase in binary alloy can be calculated using Matano's method [12] but it cannot be applied directly to intermediate phase with inhomogeneity. Heumann [13] derived an equation (Eq. (4.3)) for intermediate phases which is valid when the concentration of profile of the intermediate phase is linear throughout the phase from one end to the other end:

$$\tilde{D}_i = -\frac{1}{2t} \frac{w_i}{\Delta C_i} \int_0^{C_i^{1/2}} x dC_i$$
(4.3)

where D_i and C_i are the interdiffusion coefficient (m²/s) and the concentration of the solute *i* phase, respectively, *x* the distance from the (original) Matano interface (m), *t* the diffusion time (sec), w_i the layer thickness of *i* phase (m), ΔC_i the concentration difference of solute between the two ends of the *i* phase, and $C_i^{1/2}$ is the middle solute composition of the *i* phase. As shown in Fig. 4.1 Mg₁₇Al₁₂ and Mg₂Al₃ phases has a large inhomogeneity, so interdiffusion coefficients of these two phases were calculated using Eq. (4.3). The calculated interdiffusion coefficients are listed in Table 4.3 and also shown in Fig. 4.4 along the experimental data from previous studies.

The present interdiffusion coefficient values calculated for $Mg_{17}Al_{12}$ and Mg_2Al_3 phases were in good agreement with the results of Brenann et al. [8] but higher than the results of Funamizu et al. [5]. It should be noted that the activation energies and interdiffusion coefficients of the intermetallic phases are independent of the alignment of hcp Mg single crystal axis.

In order to investigate the anisotropic diffusion behaviour of Al in Mg, several line scans in hcp Mg from hcp Mg/Mg₁₇Al₁₂ interface toward inner hcp solution were taken for each diffusion couple sample using both EPMA-WDS with a 2 μ m spacing and 5 keV FE-SEM-EDS with a 0.3 μ m spacing. The EDS line scan was in particular helpful to examine the Al concentration profile near the interface of hcp Mg/Mg₁₇Al₁₂. When WDS and EDS results were noticeably inconsistent with each other, new areas were examined again, and in general WDS results were considered more accurate than EDS results in the evaluation of the diffusion coefficient. In all samples, the reproducibility of the Al profile in hcp Mg phase was confirmed by several line scans. As usual, the penetration depth of Al into hcp Mg increased with increasing time and temperature. Fig. 4.5 shows the concentration profile of Al in hcp Mg phase diffused along a-and c-axis at 693 K (420 °C) after 72 hrs of annealing. In general, the length of Al penetration in hcp Mg along the a-axis of the Mg crystal (on the basal plane) was slightly longer than that along the c-axis (normal to the basal plane). In few cases, the difference in the diffusion lengths was less noticeable.

4.4.2. Multiphase diffusion calculation

Diffusion coefficient of Al in hcp Mg with different directions was determined by fitting the concentration profile of Al using the diffusion equation via multiphase diffusion modeling. Diffusion modeling was done by solving Fick's second law:

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x} \left(D_m^i \frac{\partial C_m}{\partial x} \right) \tag{4.4}$$

where C_m is the concentration of component m (m = Mg and Al), t time, x distance, and D_m^i (m/s²) the diffusion coefficient for component m in i phase. The diffusion coefficient can be considered to be composition-independent only for very dilute solutions. For a solution phase containing high solute concentration like hcp Mg phase containing more than 10 mole % of Al in the Mg-Al system, the diffusion coefficient of component (D_m^i) can be composition-dependent, which can be expressed by the following equations in combination with the thermodynamic properties for a given phase [14]:

$$D_{Al}^{hcp-Mg} = D_{AlAl}^{hcp-Mg} - D_{MgAl}^{hcp-Mg}$$

$$D_{AlAl}^{hcp-Mg} = y_{Al} y_{Mg} \Omega_{Al}^{hcp-Mg} \frac{d\mu_{Al}^{hcp-Mg}}{dy_{Al}}, \quad D_{MgAl}^{hcp-Mg} = y_{Al} y_{Mg} \Omega_{Mg}^{hcp-Mg} \frac{d\mu_{Mg}^{hcp-Mg}}{dy_{Al}}$$
(4.5)

where y_{Al} and y_{Mg} are mole fractions (or called site fractions when more than two sublattices exist) of Al and Mg with $y_{Al} + y_{Mg} = 1$, Ω_{Al}^{hcp-Mg} and Ω_{Mg}^{hcp-Mg} the mobilities of Al and Mg in hcp Mg, respectively and μ_{Al}^{hcp-Mg} and μ_{Mg}^{hcp-Mg} the chemical potentials of Al and Mg in hcp Mg, respectively. Diffusion equation using a finite difference method was coded with FORTRAN language to complete the multiphase diffusion calculations.

Accuracy of diffusion simulation is highly dependent on the accuracy of the diffusion coefficient and thermodynamic data that used as input. A simple flowchart in Fig. 4.6 summarizes the diffusion modeling steps performed by the program code. Assumptions of the present numerical simulation are:

- d. Diffusion occurs one dimensionally across the diffusion bond.
- e. Solute composition of each phase at interface is constant at given temperature.
- f. The chemical composition at interface is always at equilibrium state.

In solving multiphase diffusion, the most critical part is the moving boundary problem (also known as Stefan problem) at the interface of the phase. Different approaches have been conducted by many researchers to solve the moving boundary problem [15-19]. Flexible-grid scheme / variable space network is one of the popular approaches among these in which the total grid expands to match the interface motion. When the grid expands, the concentrations at the girds must be adjusted. The most common method of shifting the grid positions and adjusting the grid concentrations is so-called a "Murray-Landis" transformation [17]. This transformation expands/shrinks the grids an amount proportional to their position from the moving boundary to maintain uniform grid spacing. The Murray-Landis transformation can be treated by either implicit or explicit finite difference methods. Many researchers have applied the Murray-Landis transformation [20-23] for the moving boundary problem arises in multiphase diffusion calculation.

In the present study, the moving boundary problem was solved by the Murray-Landis transformation [17] using explicit method. It involves the transformation of the concentration-distance profile to allow for the movement to the phase interfaces. Simulation steps followed by the substantial derivative for the i_{th} grid (i = 1, 2...n):

$$\frac{dC_{n,m}^{p}}{dt} = \frac{\partial C_{n,m}^{p}}{\partial x_{n}^{p}} \left(\frac{dx_{n}^{p}}{dt}\right) + \frac{\partial C_{n,m}^{p}}{\partial t}$$
(4.7)

where n is total number of grid at each phase and $(dx_{n,p}/dt)$ is the velocity of the n_{th} grid at p phase (phase interface). The velocities of interfaces were calculated using the four-point formula. Partial up winding was performed to remove the oscillation at the interface that may be arising due to large change in concentration gradient. The boundary conditions at the left interface of hcp Mg and right interface of fcc Al has been regarded as zero at the both boundary (zero mass transfer). The program was written to predict future concentration profile and the boundary movement at the interface between Mg and Al due to formation of β and γ intermetallic phases. The initial compositions of pure Al and pure Mg were taken as 99.99 wt% Al and 99.99 wt% Mg. The interface composition has been given as input in the program from the Mg-Al binary equilibrium phase diagram. Initially the thicknesses of β and γ phases were considered to be 0.1 μ m. Chemical potentials (μ) can be calculated from Gibbs energy functions stored in the critically evaluated/optimized thermodynamic database, Factsage-FTlite database [24]. The interface compositions of hcp Mg solid solution, Mg₁₇Al₁₂ solution, Mg₂Al₃ phase and fcc Al solution were also calculated using FactSage software with FTlite database [24]. The mobility of Ω_{Mg-hcp} was derived from the self-diffusion coefficients of Mg determined by Combronde et al. [2]:

$$D_{\perp Mg}^{hcp-Mg} = 1.75 \times 10^{-4} \exp(-137979/\text{RT})$$

$$D_{II Mg}^{hcp-Mg} = 1.78 \times 10^{-4} \exp(-138943/\text{RT})$$
(4.8)

The mobility values Ω_{Mg-fcc} and Ω_{Al-fcc} in fcc Al were taken from Yao et al. [25] and Cui et al. [26], respectively.

$$\Omega_{Mg}^{fcc-Al} = 1.49 \times 10^{-5} \exp(-118018/\text{RT})/\text{RT}$$

$$\Omega_{Al}^{fcc-Al} = 1.80 \times 10^{-5} \exp(-126719/\text{RT})/\text{RT}$$
(4.9)

4.4.3. Anisotropic diffusion coefficient of Al in hcp Mg

The Al diffusion coefficient in hcp Mg solid solution was obtained by fitting the exact concentration profile of Al for each experimental sample at given time and temperature by multiphase diffusion simulation. The calculated interdiffusion coefficients for $Mg_{17}Al_{12}$ and Mg_2Al_3 phases in Table 4.2 were used in the simulation to reproduce the growth of both phases. The optimized mobilities of Al in hcp Mg along a- and c-axis of Mg crystal from the present study are:

$$\Omega_{\perp Al}^{hcp-Mg} = 3.23 \times 10^{-7} \exp(-148955/\text{RT})$$

$$\Omega_{ll Al}^{hcp-Mg} = 6.32 \times 10^{-7} \exp(-153947/\text{RT})$$
(4.10)

In order to calculate impurity diffusion coefficient of Al in hcp Mg, Wagner's approach [27] was adopted. That is, the impurity diffusion coefficient was obtained by extrapolating the interdiffusion coefficients of solute in hcp Mg solid solution (or diffusion coefficient of Al in hcp Mg) very carefully to zero percent of Al in hcp Mg solid solution. The impurity diffusion coefficient values for Al in hcp Mg from the present experimental study are:

$$D_{\perp Al}^{hcp-Mg} = 4.86 \times 10^{-3} \exp(-154484/\text{RT})$$
$$D_{II Al}^{hcp-Mg} = 9.51 \times 10^{-3} \exp(-159476/\text{RT})$$
(4.11)

The present Al diffusion coefficients are plotted in Fig. 4.7 along with the previous results derived from polycrystalline experiments. Our diffusion coefficients of Al are slightly lower than those of Brenann et al. [7] and Moreau et al. [4]. The diffusion coefficient of Al along a-axis is slightly higher (1.26~1.41 times) than that along c-axis. As temperature increases, the difference in the diffusion coefficients becomes smaller.

The diffusion coefficient of Al in hcp Mg along its a-axis is slightly faster than that along c-axis: $D_{\perp}/D_{\parallel} = 1.41$ at 638 K (365 °C) and 1.26 at 693 K (420 °C). Similar trends were observed for impurity elements such as Cd, In, Sn and Sb by Combronde et al. [28] using the tracer diffusion technique: the diffusion coefficients of these elements along Mg a-axis were determined to be higher than that of c-axis (1.0 to 1.3 times between 733 and 903 K (460 and 630 °C)). In the case of Ag, however, the diffusion along the c-axis was about 2.4 times faster than that along the a-axis at 753 K (480 °C) and became smaller with increasing temperature (about 1.6 times at about 912 K (639 °C)). The present activation energies of the diffusion of Al in hcp Mg along the a-and c-axis are 154.48 \pm 3.86 kJ/mol and 159.48 \pm 2.45 kJ/mol, respectively. These activation energies are similar to the experimental value of Brenann et al. [7], 156.3 kJ/mol, for polycrystalline Mg.

Ganeshan et al. [9] performed the first principles calculations for the impurity diffusion coefficients of Al in Mg. According to their calculations, the diffusion along the basal plane (a-axis) is about $1.6 \sim 1.8$ times faster than that along normal direction of the basal plane (c-axis) between 638 and 693 K (365 and 420 °C). However, the calculated diffusion coefficients of Al are lower than the values from our experiments by about one or two order of magnitude as it can be seen in Fig. 4.6 (b). The main difference was from pre-factor of diffusion coefficients in Eq. (4.11). The activation energies of Al diffusion in Mg estimated from the first principles calculations are 137 kJ and 143 kJ along the basal plane (a-axis) and normal direction of the basal plane (c-axis), respectively, which are also much lower than our values derived from the single crystal experimental data. Interestingly, the difference in the activation energies between

two directions from the first principles calculations (6 kJ) is similar to that from our study (5 \sim 6 kJ).

Most of alloying elements studied in literature tend to show faster diffusion along the a-axis of hcp Mg than along the c-axis of hcp Mg. However, the solute such as Ag [27] shows the opposite trend. It is hard to explain clearly why the diffusion of Al through basal plane is faster than the one normal to the basal plane. As mentioned by Ganeshan et al. [9], the diffusions of Al along a-and c-axis of hcp Mg crystal involve the solute or vacancy jumps within the basal plane and outside to the adjacent basal plane, respectively. At least, it could be told from the present study that the energy barrier for jumping along the c-axis is higher than that along the a-axis (see the activation energy in Eq. (4.11)).

4.5. Summary

The anisotropic diffusion behavior of Al in hcp Mg was experimentally investigated using the diffusion couple technique with single crystal Mg. The diffusion coefficient of Al within the basal plane is about 1.3 times faster than that along the normal direction of the basal plane between 638 and 693 K (365 and 420 °C). The activation energy for Al diffusion along the c-axis of hcp Mg is about 4.5 % higher than that of the a-axis. The anisotropy of the Al diffusivity becomes smaller with increasing temperature. The interdiffusion coefficients of Mg₁₇Al₁₂ and Mg₂Al₃ solid solutions were also derived and were in good agreement with the previous studies.

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Terretorie	T :	Lengt	n of the Inte	ermetallics	Distance from the original interface*						
Temperature	Time		(μι	m)		(µm)					
K (°C)	(°C) (hrs)		₇ Al ₁₂	Mg	$_2Al_3$	Mg ₁₇	$_{7}\mathrm{Al}_{12}$	Mg ₂ Al ₃			
Mg single orienta	Mg single crystal orientation		c-axis ⁺	a-axis [#]	c-axis ⁺	a-axis [#]	c-axis ⁺	a-axis [#]	c-axis ⁺		
	48	26.3	27	136	136	149	152	122.7	125		
638 (365)	72	40	33	197	193	218	202	178	169		
	94	46	38	234	230	260	247	214	209		
663 (390)	72	68	65.8	267	264	316	314	244	243		
	94	82	79	309	306	340	336	258	257		
	48	67	69	223	229	270	277	203	208		
673 (400)	72	90	89	288	285	357	345	267	256		
	94	92	94	329	324	381	388	289	296		
	48	84	82	248	245	302	306	218	224		
693 (420)	72	151	136	317	313	444	419	293	284		
	94	186	150	370	370	516	486	332	336		

Table 4.1. Summary of the experimental results for Mg single crystal and Al diffusion couples.

*until the end of the layer in Mg side

[#]diffusion along the a-axis direction in single crystal hcp Mg

⁺diffusion along the c-axis direction in single crystal hcp Mg

Orientation	Mg ₁	₇ Al ₁₂	Mg	Reference	
	$k_o^2(m^2/s)$	Q (kJ)	$k_o^2(m^2/s)$	Q (kJ)	_
a-axis	1.33	175.68	5.0×10^{-8}	67.63	Present Study
c-axis	2.53	180.34	6.0×10^{-8}	68.83	
Polycrystalline	0.36	165.1	2.2×10^{-6}	85.9	Brenann [8]
Polycrystalline	6.281	227.57	8.0×10^{-7}	83.23	Brubaker [6]
Polycrystalline	0.011	149.99	3.0×10^{-8}	65.25	Funamizu [5]

Table 4.2. Growth constants and for $Mg_{17}Al_{12}$ and Mg_2Al_3 phases from the present study in comparison to the previous studies.

Table 4.3. Interdiffusion coefficients for $Mg_{17}Al_{12}$ and Mg_2Al_3 phases from the present study in comparison to the previous studies.

Orientation	Mg ₁₇ Al ₁	2	Mg ₂ Al	Reference		
	$D_o(m^2/s)$	Q (kJ)	$D_o(m^2/s)$	Q (kJ)		
a-axis	$3.59 (\pm 0.82) \times 10^{-5}$	109.9396 (±2.18)	$2.96 (\pm 1.69) \times 10^{-6}$	78.9177(±8.43)	Present	
c-axis	$2.89 (\pm 3.24) \times 10^{-5}$	109.2949 (±3.13)	$1.55 (\pm 3.07) \times 10^{-6}$	76.2443(±2.37)	Study	
Polycrystalline	1.8×10^{-3}	129.7	9.6×10 ⁻⁶	84.8	Brenann [8]	
Polycrystalline	9.9(+11.9;-5.4)×10 ⁻⁵	117.57(± 4.18)	$2.4(+3.3;-1.4) \times 10^{-8}$	56.90 (± 4.60)	Funamizu [5]	



Fig. 4.1. Diffusion couple experiment with single crystal Mg: (a) Interface microstructure of diffusion couple (SEM BSE image) after 72 hrs annealing at 693 K (420 °C), (b) Al concentration profile (WDS line scan) through the interface. (c), (d) are the examples of XRD pole figures of (0001) and (1000) planes in Mg single crystal, respectively.



(a)



Fig. 4.2. Intermetallic layer thicknesses vs. square root of diffusion anneal time at 400°C (a) along a-axis, (b) along c-axis.







Fig. 4.3. Variation of the growth constants of intermediate phases (a) $Mg_{17}Al_{12}$ phase and (b) Mg_2Al_3 phase with temperature in comparison to the previous studies [5, 6, 8].



(b)

Fig. 4.4. Variation of the interdiffusion coefficients of intermediate phases (a) $Mg_{17}Al_{12}$ phase and (b) Mg_2Al_3 phase with temperature in comparison to the previous studies [5, 8].



Fig. 4.5. Experimental Al concentration profiles in Mg single crystals diffused for 72 hrs at 693 K (420 °C).



Fig. 4.6. Flowchart for diffusion simulation in multiphase system.



Fig. 4.7. Variation of Al impurity diffusion coefficients in hcp Mg along its a- and c-axis directions with temperature. (a) present experimental data, and (b) comparison with the previous data derived from polycrystalline samples [4, 7] and the first principles calculations [9].

Chapter – 5

Investigation of anisotropic diffusion behavior of Zn in hcp Mg and interdiffusion coefficients of intermediate phases in the Mg-Zn system

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Dr. Y. M. Kim assisted as a post-doctoral fellow in developing the multiphase diffusion program. Prof. T. K. Ha produced the Mg single crystals necessary for the experimental study. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision. All the Co-Authors provided valuable suggestions and comments and reviewed the manuscript before submission.

5.1 Abstract

The anisotropic diffusion behavior of Zn in hcp Mg was for the first time experimentally investigated using diffusion couple experiments with Mg single crystals at temperatures between 553 and 603 K (280 and 330 °C). The diffusion coefficients determined from Zn concentration profiles in hcp Mg single crystals are: $D_{\perp Zn}^{hcp-Mg} = 4.98 \times 10^{-5} \exp(-132725/\text{RT}) \text{ m}^2/\text{s}$ along the basal plane and $D_{II-Zn}^{hcp-Mg} = 7.33 \times 10^{-5} \exp(-135488/\text{RT}) \text{ m}^2/\text{s}$ normal to the basal plane. The diffusion coefficient of Zn along the basal plane is about 1.23 times higher than the one normal to the basal plane at the experimental temperatures. Interdiffusion coefficients of Mg₂Zn₃, MgZn₂ and Mg₂Zn₁₁ were experimentally determined for the first time. In addition, the interdiffusion coefficients of Mg₁₂Zn₁₃ and Mg₅₁Zn₂₀ were calculated from a multiphase diffusion model.

Keywords: Magnesium alloy, zinc, intermetallics, diffusion, diffusion couple.

5.2. Introduction

The number of industrial applications of Mg-based alloys in the aerospace, automotive and electronic industries is increasing rapidly thanks to the performances and light weight of such alloys. In automotive industries, Mg-based alloys are used as much as possible because they have a high specific strength. Zn is one of the common alloying elements in Mg which is well known to improve its strength by precipitation hardening. However, the high temperature solute behavior of Mg-based alloys is still unknown. As a consequence, no systematic study on solute behavior exists. Diffusion is critically important to describe physical properties such as solidification, precipitation, dissolution, oxidation, corrosion, and creep of Mg-based alloys at high temperatures. Systematic studies on diffusion can help to find reliable parameters needed in high temperature processes so that the final product possesses the desired microstructure and mechanical properties.

Magnesium has an hcp crystal structure (c/a ratio = 1.6236, where c/a is the ratio of Mg lattice constants). Therefore, the diffusion of alloying elements in hcp Mg shows anisotropic behavior depending on the orientation of the Mg crystal. Shewmon [1] and Combronde et al. [2] investigated Mg self-diffusion using a radiotracer serial sectioning method with a Mg single crystal and concluded that self-diffusion perpendicular to the c-axis of the lattice is higher than that along the c-axis. Mantina [3] determined Mg self-diffusion coefficients from first principles calculations and arrived at the same conclusion. Although Lal [4] and Cermak et al. [5] measured Zn diffusion in polycrystalline Mg, no anisotropic Zn diffusion was experimentally determined. Lal [4] measured the impurity (radiotracer serial sectioning) diffusion of Zn in polycrystalline Mg between 740 and 893 K (467 and 620 °C) using the radio tracer ⁶⁵Zn. On the other hand, Cermak et al. [5] employed both radiotracer serial sectioning and residual activity to investigate the diffusion of Zn in polycrystalline Mg between 648 and 848 K (375 and 575 °C). Recently, Ganeshan et al. [6] performed first principles calculations to estimate impurity diffusion coefficients of Al, Zn, Sn and Ca in dilute Mg alloy using an 8-frequency model within the local density approximation (LDA). They reported that the directional diffusion coefficient of Zn in Page | 96

hcp Mg along the c-axis is 18.11 to 13.78 times higher than that along the a-axis between 400 and 833 K (127 and 560 °C), but the calculated diffusion coefficients were about two orders of magnitude lower than the polycrystalline experimental values of Lal [4] and Cermak et al. [5]. The LDA results for Mg self-diffusion and Zn self-diffusion by Ganeshan et al. [7] also shows similar trends while compared with experimental data and underestimate diffusion coefficients especially at high temperatures.

Sakakura et al. [8] also conducted a Mg-Zn diffusion couple experiment between 473 and 573 K (200 and 300 °C) and observed the intermediate compounds MgZn₂ and Mg₂Zn₁₁ at the interface of the diffusion couple. Using experimental data, they calculated growth constants and interdiffusion coefficients of Zn for the intermediate compounds. Very recently, Brennan et al. [9] also conducted Mg-Zn diffusion couple experiments between 568 and 598 K (295 and 325 °C), and reported four intermediate phases, Mg₅₁Zn₂₀, Mg₂Zn₃, MgZn₂ and Mg₂Zn₁₁, at the interface. They calculated the activation energies for growth constants of the MgZn₂ and Mg₂Zn₃ phases. Polycrystalline Mg samples were used in both diffusion couple experiments.

Recently, the present authors used diffusion couple experiments with Mg single crystals to determine the anisotropic diffusion behavior of Al in hcp Mg [10]. The anisotropic diffusion coefficients of Al were calculated from the diffusion profiles of Al along the a- and c-axis of hcp Mg single crystals. In the present study, the anisotropic diffusion behavior of Zn in Mg was experimentally studied with the same technique. In addition, the interdiffusion coefficients and growth constants of intermetallic phases in the Mg-Zn system were determined.

5.3. Experimental

Mg single crystals were produced using a modified Bridgman furnace located at Gangneung-WonJu University, Korea. Each Mg sample was identified as a single crystal using Electron Page | 97 Backscattered Diffraction (EBSD) and X-Ray Diffraction (XRD). Unfortunately, the direction of each Mg single crystal was not well controlled during the growth process because no pre-single crystal seed was used in the experiments. Therefore, all the samples (about 15 cm in length and 10 mm in diameter) produced in the Bridgman furnace were examined to check the direction of the single crystals using Bruker D8 XRD pole figure measurements. Then, each crystal was cut very carefully using a Buehler IsoMet diamond saw with a specially designed cutting jig to obtain single crystals with the surface parallel/perpendicular to the basal plane of Mg. In order to avoid surface deformation, a very low cutting speed was applied. Polycrystalline pure Zn (99.99%, Alfa Aesar) ingot was sectioned into a small rectangle (15 mm x 15 mm x 10 mm). It was then cut into halves using a low speed diamond saw and ground to make half-circular discs. These were annealed at 623 K (350 °C) under high purity Ar (5N) to relieve any stress produced during the sample preparation and to obtain a large grain size. The grain size of Zn was larger than 1000 µm. The Mg and Zn samples were then polished down with 0.25 µm diamond suspension to obtain fine flat surfaces. The orientation of each Mg single crystal was reconfirmed by an XRD pole figure measurement before the diffusion experiment. Discs made of Mg and Zn were tied with a stainless steel clamp well enough to make sure that the surfaces of the samples were in perfect contact with each other.

Diffusion couple experiments were carried out in a gas tight tube furnace filled with high purity argon. In order to minimize the oxidation of the sample, the diffusion couple sample was rapped with Ta foil and the argon gas was flowed at a rate of 10 ml/min during the annealing experiments. The temperature of the sample was measured using a K-type thermocouple just above the diffusion couple sample. The annealing experiments were done between 553 and 603 K (280 and 330 °C) for 4 to 20 days to make sure that all intermetallic phases developed enough layers in the solid state. After the annealing, samples were taken out from the furnace and quickly quenched in cold water. The mounted diffusion couple samples were cut exactly perpendicular to the diffusion contact plan using a low speed diamond saw and polished with 0.1 µm colloidal silica suspension. Intermetallic phases and Mg and Zn solid solution phases were examined using a Philips XI-30 Field Emission-Scanning Electron Microscope (FE-SEM) and a JEOL 8900 Electron Probe Micro Analyzer (EPMA). The Zn concentration profiles through the

interface and inside the hcp Mg were measured by EPMA using Wavelength Dispersive Spectroscopy (WDS) at 10 to 15 keV, 20 nA beam current and 15 mm working distance.

5.4. Results and discussion

The backscattered electron image of a diffusion couple sample annealed at 593 K (320 °C) for 4 days is shown in Fig. 5.1 (a) together with its Zn concentration profile determined by EPMA-WDS through the diffusion couple interface in Fig. 5.1 (b). Backscattered images confirmed the existence of four intermetallic phases (the stoichiometric Mg₁₂Zn₁₃, Mg₂Zn₃ and Mg₂Zn₁₁ compounds and the MgZn₂ solid solution) at 553, 573 and 593 K (280, 300 and 320 °C). In the case of the samples annealed at 603 K (330 °C) (see Figs. 5.1 (c) and (d)), a continuous layer of Mg₅₁Zn₂₀, which has a very small thermal stability range between 598 and 620 K (325 and 347 °C), was also observed adjacent to the Mg side. The thermodynamic properties and stability regions of all these phases can be found in the critically assessed Mg-Zn phase diagram [11]. The presence of the Kirkendall effect [12] was observed by optical microscopy and also confirmed by WDS and EDS. Based on EPMA-WDS line scans, the exact interfaces between hcp Mg, intermetallic phases, and Zn were determined and the composition variations in the intermetallic phases were measured. Position of the Matano plane [13] was identified from the WDS line scan of each sample to find the interdiffusion coefficient. Most of the intermetallic phases formed toward the Mg side because the diffusion of Zn in hcp Mg is faster than that of Mg in hcp Zn. Zn has a lower melting point (692.68 K (419.53 °C)) than Mg (923 K (650 °C)), consequently, it may require less activation energy for Zn to migrate. In addition, the atomic radius of Zn (134 pm) is smaller than Mg (160 pm) which can allow Zn to move easily in hcp Mg than Mg in hcp Zn. Experimental results are summarized in Table 5.1.

5.4.1. Growth constants and interdiffusion coefficients of intermetallic phases

The growth constants of $Mg_{12}Zn_{13}$, Mg_2Zn_3 , $MgZn_2$ and Mg_2Zn_{11} were determined to find the growth kinetics of the intermediate phases. The experimental growth rates of all intermediate

phases followed typical parabolic trends with time. The parabolic growth constant based on diffusion-controlled growth can be calculated with:

$$x = k\sqrt{t} \tag{5.1}$$

where x is the thickness of the intermetallic phase, t is the annealing time and k is the growth constant of which temperature dependency can be expressed by the following Arrhenius relationship:

$$k = k_{p} \exp(-Q/RT) \tag{5.2}$$

where k_o (m/s^{0.5}) is the pre-exponential factor, R (J/mol-K) the gas constant, Q (J) the activation energy, and T the annealing temperature in Kelvin.

Eq. (5.1) assumes that the nucleation time of the intermetallic phases is negligible in comparison with the present annealing time. In order to prove that this is a valid assumption, the layer thickness of intermetallic phases is reported against the square root of time in Fig. 5.2. As it can be seen in the figure, the linear fit to the experimental data points can reach the origin, which proves that the nucleation time is negligible compared with the annealing time. Therefore, the calculations of the growth constant, and diffusivities of intermetallic phases and Zn in Mg from our study are accurate.

The calculated growth constants and activation energies of $Mg_{12}Zn_{13}$, Mg_2Zn_3 , $MgZn_2$ and Mg_2Zn_{11} are listed in Table 5.2 and presented in Fig. 5.3. No noticeable differences in the growth constants of intermetallics were found depending on the orientation of the Mg single crystals.

The growth constants of Mg_2Zn_{11} and $MgZn_2$ are in good agreement with the previous results of Sakakura et al. [8] and Brenann et al. [9] at high temperatures. At low temperatures, however, our experimental values are slightly lower than the previous results [8, 9].

The interdiffusion coefficients of intermetallic phases were calculated using the Heumann-Matano's method [13, 14] which is valid when the concentration profile of the intermediate phase is linear throughout the layer of the phase from one end to the other end:

$$\tilde{D}_{i} = -\frac{1}{2t} \frac{w_{i}}{\Delta C_{i}} \int_{0}^{C_{i}^{1/2}} x dC_{i}$$
(5.3)

where D_i and C_i are the interdiffusion coefficient (m²/s) and the concentration of the solute *i* phase, respectively, *x* the distance from the (original) Matano interface (m), *t* the diffusion time (sec), w_i the layer thickness of *i* phase (m), ΔC_i the concentration difference of solute between the two ends of the *i* phase, and $C_i^{1/2}$ is the middle solute composition of the *i* phase.

As can be seen in Fig. 5.1, thick layers of Mg₂Zn₃, MgZn₂ and Mg₂Zn₁₁ with linear concentration profiles enables application of the Heumann-Matano method to calculate their interdiffusion coefficients. Unfortunately, the layers of Mg₁₂Zn₁₃ and Mg₅₁Zn₂₀ were too thin to determine the interdiffusion coefficient from the Heumann-Matano's method and the coefficients were thus calculated using the multiphase diffusion simulation, discussed in section 3.2, for each sample. The interdiffusion coefficient of Mg₅₁Zn₂₀, which was only observed at 603 K (330 °C), was calculated to be 6.56 (\pm 0.88) ×10⁻¹⁴ m²/s. The interdiffusion coefficients of all other intermetallic phases obtained in the present study are listed in Table 5.3 and also illustrated in Fig. 5.4.

The interdiffusion coefficient of $MgZn_2$ is in good agreement with the previous results of Sakakura et al. [8], whereas for the Mg_2Zn_{11} phase, our value is slightly lower than theirs. It is hard to explain the difference in the interdiffusion coefficients of Mg_2Zn_{11} because the growth rate in our work is very similar to that of Sakakura et al. [8], especially at 573 K (300 °C). The difference may come from the calculation using the Matano's method in Eq. (5.3) which requires accurate boundary composition for the Mg_2Zn_{11} phase.

5.4.2. Multiphase diffusion simulation

In order to investigate the anisotropic diffusion behaviour of Zn in hcp Mg, several line scans in hcp Mg were performed for each diffusion couple sample using EPMA-WDS with 1.5-2.0 μ m spacing. In all samples, the reproducibility of the Zn profile in hcp Mg was confirmed by several line scans. As usual, the penetration depth of Zn into hcp Mg increased with increasing time and temperature. The concentration profile of Zn in hcp Mg diffused along the a- and c-axis at 593 K (320 °C) after 4 days of annealing is depicted in Fig. 5.5. In general, the length of Zn penetration in hcp Mg along the a-axis is slightly longer than along the c-axis. In a few cases, the difference in the diffusion lengths was less noticeable.

Diffusion coefficient of Zn in hcp Mg along the a- and c-axis were determined by fitting the concentration profile of Zn using the diffusion equation via multiphase diffusion modeling. Diffusion modeling was done by solving Fick's second law:

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x} \left(D_m^i \frac{\partial C_m}{\partial x} \right)$$
(5.4)

where C_m is the concentration of component *m*, *t* the time, *x* the distance, and D_m^i (m/s²) the diffusion coefficient for component *m* in *i* phase. For an intermetallic phase, the interdiffusion coefficient is used in Eq. (5.4). For a solution phase containing high solute concentration, like the hcp Mg phase containing more than 5 mole % of Zn in the Mg-Zn system, the diffusion coefficient of the component (D_i^m) can be composition-dependent, which can be expressed by the following equations in combination with the thermodynamic chemical potential (μ) [15]:

$$D_{Zn}^{hcp-Mg} = D_{ZnZn}^{hcp-Mg} - D_{MgZn}^{hcp-Mg}$$

$$\tag{5.5}$$

$$D_{ZnZn}^{hcp-Mg} = y_{Zn} y_{Mg} \Omega_{Zn}^{hcp-Mg} \frac{d\mu_{Zn}^{hcp-Mg}}{dy_{Zn}}$$
(5.6)

$$D_{MgZn}^{hcp-Mg} = y_{Zn} y_{Mg} \Omega_{Mg}^{hcp-Mg} \frac{d\mu_{Mg}^{hcp-Mg}}{dy_{Zn}}$$
(5.7)

where y_{Zn} and y_{Mg} are the mole fractions (site fractions when more than two sublattices exist) of Zn and Mg with $y_{Zn} + y_{Mg} = 1$, Ω_{Zn}^{hcp-Mg} and Ω_{Mg}^{hcp-Mg} are the mobility of Zn and Mg in hcp Mg, respectively. μ_{Zn}^{hcp-Mg} and μ_{Mg}^{hcp-Mg} are the chemical potentials of Zn and Mg in hcp Mg, respectively.

The diffusion equation using a finite difference method (FDM) was coded with FORTRAN language to complete the multiphase diffusion calculations. In solving multiphase diffusion, the most critical part is the moving boundary problem (also known as Stefan problem) at the interface of the phases. Different approaches have been designed by many researchers to solve the moving boundary problem [16-20]. The flexible-grid scheme/variable space network is one of the most popular approaches in which the total grid expands/shrinks to match the interface motion. The most common method of shifting the grid positions and adjusting the grid

concentrations is the so-called "Murray-Landis" transformation [18]. The Murray-Landis transformation has been applied by many researchers [21-24] to moving boundary problems occurring in multiphase diffusion calculations. In the present study, the moving boundary problem was also treated by the Murray-Landis transformation using an explicit method.

Initially, the thicknesses of intermediate phases were considered to be 0.1 μ m. Chemical potentials (μ) were calculated from the Gibbs energy functions stored in the critically evaluated/optimized thermodynamic database FactSage FTlite [11]. The interface composition of hcp Mg solid solution adjacent to Mg₁₂Zn₁₃ (Mg₅₁Zn₂₀ at 603K (330 °C)) was also calculated with the FTlite database because the interface composition of hcp Mg determined in the experiments can interfere with the adjacent phase at its boundary. The details of the multiphase diffusion simulation can be found elsewhere [10, 25].

5.4.3. Anisotropic diffusion coefficient of Zn in hcp Mg

The multiphase diffusion simulation was employed to reproduce the growth of phases in diffusion couple experiments. The interdiffusion coefficients of Mg₁₂Zn₁₃, Mg₂Zn₃, MgZn₂ and Mg₂Zn₁₁ obtained in the present study (Table 5.3) were used in the simulation to reproduce the growth of all intermediate phases. The Zn diffusion coefficient in hcp Mg solid solution was obtained to fit the exact concentration profile of Zn in each experimental sample. In the simulation, the mobilities of Ω_{Mg}^{hcp-Mg} ($\Omega_{Mg}^{hcp-Mg} = D_{Mg}^{hcp-Mg}/RT$) depending on the orientation of Mg were derived from the self-diffusion coefficients of Mg determined by Combronde et al. [2]: $D_{\perp Mg}^{hcp-Mg} = 1.75 \times 10^{-4} \exp(-137979/RT)$ and $D_{H}^{hcp-Mg} = 1.78 \times 10^{-4} \exp(-138943/RT)$. The mobility value Ω_{Zn}^{hcp-Zn} in hcp Zn solution was taken from Cui et al. [26]: $\Omega_{Zn}^{hcp-Zn} = 2.07 \times 10^{-5} \exp(-94975/RT)/RT$. The mobility of Mg in hcp Zn Ω_{Mg}^{hcp-Zn} was assumed to be the same as Ω_{Zn}^{hcp-Zn} .

The optimized mobilities of Zn in hcp Mg perpendicular and parallel to the c-axis of Mg crystal from the present study are:

$$\Omega_{\perp Zn}^{hcp-Mg} = 3.0 \times 10^{-10} \exp(-127928/\text{RT})$$
(5.8)

$$\Omega_{II-Zn}^{hcp-Mg} = 1.0 \times 10^{-9} \exp(-130690/\text{RT})$$
(5.9)

The impurity diffusion coefficient was obtained by extrapolating the interdiffusion coefficients of solute in hcp Mg solid solution (or diffusion coefficient of Zn in hcp Mg) very carefully to zero percent of Zn in hcp Mg solid solution. The impurity diffusion coefficients for Zn in hcp Mg obtained from the present study are (although in principle $D = RT \Omega$, diffusivity is typically expressed as an Arrhenius equation; so we prefer to give the conventional equation after the recalculation from the above mobility values):

$$D_{\perp Z_n}^{hcp-Mg} = 4.98 \times 10^{-5} \exp(-132725/\text{RT})$$
 (5.10)

$$D_{II}^{hcp-Mg} = 7.33 \times 10^{-5} \exp(-135488/\text{RT})$$
(5.11)

The present Zn diffusion coefficients are shown in Fig. 5.6. The diffusion coefficient of Zn in hcp Mg along the a-axis is slightly higher (1.17 to 1.23 times) than along the c-axis. As the temperature increases, the difference in the diffusion coefficients becomes smaller: $D\perp/D_{\parallel} = 1.23$ at 553 K (280 °C) and 1.17 at 603 K (330 °C). Similar trends were observed for other impurity elements such as Cd, In, Sn and Sb by Combronde et al. [27] using the radiotracer serial sectioning technique: the diffusion coefficients of the elements along the Mg a-axis were found to be 1.0 to 1.3 times higher than that of c-axis between 733 and 903 K (460 and 630 °C). The present authors [10] also reported that the diffusion of Al in hcp Mg along the a-axis is faster

than along the c-axis using Mg single crystal diffusion couple experiments: $D_{\perp}/D_{\parallel} = 1.33$ at 638 K (365 °C) and 1.18 at 693 K (420 °C).

In comparison to the previous data of Lal [4] and Cermak et al. [5] who used a radiotracer serial sectioning method with polycrystalline Mg, the present experimental diffusion coefficients of Zn are lower by almost one order of magnitude. Such a large difference is difficult to explain. One possibility would be grain boundary diffusion in the polycrystalline samples which may induce faster diffusion of Zn in hcp Mg. However, grain boundary diffusion is typically known to be more dominant at low temperatures rather than at high ones as in the case of the experiments described by Lal [4] and Cermak et al. [5]. When the diffusion coefficients by Lal and Cermak et al. were used in the multiphase diffusion simulation, the diffusion depth of Zn in hcp Mg became about 3 times longer than the present experimental data. We also performed annealing experiments for the as-cast Mg-Zn samples (Zn = 1.5, 4.0 and 5.5 wt. %) at 603 and 673 K (330 and 400 °C). The diffusion coefficients reported by Lal [4] and Cermak et al. [5] overestimated the diffusion of Zn during the annealing of the samples, while our new data can well reproduce the annealed Zn profiles.

It is very interesting that the slopes of the diffusion coefficients depicted in Fig. 5.6 are similar for all the experiments, which means that the activation energy of diffusion is comparable in any case. The present activation energies of the diffusion of Zn in hcp Mg along the a- and c-axis are 132.73 ± 1.45 kJ/mol and 135.49 ± 1.62 kJ/mol, respectively. These activation energies are similar to the experimental values of Cermak et al. [5], 126.79 kJ/mol (radiotracer serial sectioning) and 132.61 kJ/mol (residual activity), for polycrystalline Mg, although the absolute values of diffusivity are different. The activation energy of Lal [4], 119.73 kJ/mol (tracer section), is slightly lower than that of the present study. It should be also noted that the activation energies of Zn are similar to those for Al in hcp Mg and Mg self-diffusion.

Ganeshan et al. [6] performed first principles calculations using a 8-frequency model within the LDA for the impurity diffusion coefficients of Zn in Mg. According to their calculations, the diffusion normal to the basal plane direction (c-axis) is about 14.17 to 15.66 times faster than that along the basal plane direction (a-axis) in the temperature range of 603 to 553 K (330 and 280 °C). This is inconsistent with the present experimental data. The same problem was also found in the first principle calculations of Al diffusion in Mg by Ganeshan et al. [6]. These differences may be due to the underestimation of the diffusion coefficient by LDA which was explained by Ganeshan et al. [7]. Wrobel et al. [28] also argued that LDA sometimes underestimates diffusion whereas generalized gradient approximation (GGA) overestimates it. That is, the GGA and LDA results, when put together, can provide a good upper-lower limit of the diffusivity as explained by Ganeshan et al. [7]. As the PBEsol technique [29] tends to improve the overall agreement with experimental data on bulk properties due to the impurity diffusion coefficients of zn in Mg using the PBEsol technique may produce better agreement with the present experimental data than with GGA and LDA.

5.5. Summary

Diffusion couple experiments with Mg single crystals were performed to determine the anisotropic diffusion behavior of Zn in hcp Mg and interdiffusion coefficients of intermediate phases. The interdiffusion coefficients of $Mg_{12}Zn_{13}$, Mg_2Zn_3 , $MgZn_2$, Mg_2Zn_{11} and $Mg_{51}Zn_{20}$ were properly determined for the first time.

Diffusion coefficients determined from the present diffusion couple experiments are based on concentration profiles obtained by quantitative EPMA-WDS line scans. The reproducibility observed in the composition of each sample was confirmed by several line scan analyses. Moreover, the diffusion coefficients measured at each temperature were averaged for the samples annealed at three different time spans. Care was taken to avoid oxidation at the diffusion

interface in the entire course of experiments. Small discontinuous oxides were observed at the interface but they were found to be unimportant in the determination of diffusion coefficients. The experimental error range for each diffusion coefficient is reported.

The anisotropic diffusion behavior of Zn in hcp Mg was also experimentally determined for the first time. The diffusion coefficient of Zn along the basal plane is about 1.23 times faster than along the normal direction of the basal plane between 553 and 603 K (280 and 330 °C). This is about one order of magnitude lower than previously reported experimental data using polycrystalline Mg. The present diffusion coefficient of Zn in hcp Mg is almost similar to the one of Mg self-diffusion but slightly lower than the Al diffusion coefficient in hcp Mg.

5.6 Acknowledgements

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5.7 References

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Т	Orientation of Mg		4 0	days		10 days				20 days				Matano plane location*		
(K)	crystal	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	4 days	10 days	20 days
553	a-axis	9.5	91.1	10.2	0.339	21.7	143	15.2	0.539	23.8	179	28.5	0.685	29	49	61
	c-axis	9.64	91.3	10.8	0.361	21.5	146	15	0.574	23.9	173	30.2	0.731	27	51	63
T (K)	Orientation of Mg		4 0	days			5 di	ays			6 da	iys		Matano plane location*		
	crystal	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	$Mg_{12}Zn_{13}$	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	Mg_2Zn_{11}	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	4 days	days	days
573	a-axis	16.8	137	16.9	0.57	22.7	151	18.3	0.714	24.5	164	21.8	0.804	42	50	54
	c-axis	16.8	139	16.1	0.553	22.8	148	16.9	0.691	24.6	169	21.7	0.877	45	48	52
		L	I	L			L	I				I				

Table 5.1. Summary of the present experimental results of the diffusion couples. Layer thicknesses of intermetallics in μ m.

T Orientation of Mg			4 0	days		8 days				12 days				Matano plane location*		
(K)	crystal	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Mg ₁₂ Zn ₁₃	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	4 days	8 days	12 days		
593	a-axis	27.2	180	31.4	0.749	37.1	234	43.9	1.22	58.2	295	57	1.64	55	67	96
	c-axis	29.5	183	32.3	0.876	36.6	222	43.2	1.39	56.9	287	56.3	1.59	62	65	99
Т	Orientation of Mg			5 days		L			9 days	1	L		Matano pl locatior			
(K)	crystal	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	Mg ₅₁ Zn ₂₀	Mg ₂ Zn ₁₁	MgZn ₂	Mg ₂ Zn ₃	Mg ₁₂ Zn ₁₃	Mg ₅₁ Zn ₂₀			5 days	9 days	
603	a-axis	33.5	238	44.6	1.61	4.58	70.5	305	52.9	2.1	7.51			72	103	
	c-axis	34.1	234	48.1	1.6	4.51	71.3	303	53.4	2	7.22			69	102	
	I			L	I		I	I		1				I		

Table 5.2. Growth constants of Mg_2Zn_{11} , $MgZn_2$, Mg_2Zn_3 and $Mg_{12}Zn_{13}$ from the present investigation compared to previous studies [8, 9].

Orientation	Mg ₂ Zn ₁₁		MgZn ₂		Mg_2Zn_3		Mg ₁₂ Z	2n ₁₃	Reference
	$k_{o}^{2}(m^{2}/s)$	Q(kJ)	$k_{o}^{2}(m^{2}/s)$	Q(kJ)	$k_{o}^{2}(m^{2}/s)$	Q(kJ)	$k_{o}^{2}(m^{2}/s)$	Q(kJ)	
a-avis	1.80(±0.14)	134.278	9.50(±0.71)	92.165	1.70(±0.95)	133.806	4.00	154.689	
u-uAIS	$\times 10^{-3}$	(± 0.235)	$\times 10^{-6}$	(±1.587)	$\times 10^{-3}$	(±3.138)	$\times 10^{-5}$	(±7.819)	D
									Present
	3.65(±1.77)	137.229	1.63(±6.35)	92.844	7.35(±3.89)	140.638	5.00(±4.24)	148.412	Study
c-axis	$\times 10^{-3}$	(± 2.175)	×10 ⁻⁵	(±1.651)	×10 ⁻³	(±2.998)	×10 ⁻⁵	(±5.056)	
D = 1 = = = = = = = = = = = = = = = = =	$20 10^{-9}$	(0.252	2.0.10-7	72 222					
Polycrystalline	2.0×10	68.253	3.0×10	/3.233	-	-	-	-	[8]
Polycrystalline	-	-	1.1×10 ⁵	207	2.8×10^{-6}	105	-	-	[9]

Table 5.3. Interdiffusion coefficients of Mg_2Zn_{11} , $MgZn_2$, Mg_2Zn_3 and $Mg_{12}Zn_{13}$ from the present investigation compared to the previous study [8].

Orientation	Mg ₂ Zn ₁₁		MgZ	n ₂	Mg ₂ Zı	13	Mg	Reference	
	$D_o (\mathrm{m^2/s})$	Q(kJ)	$D_o (\mathrm{m^2/s})$	Q(kJ)	$D_o (\mathrm{m^2/s})$	Q(kJ)	$D_o (\mathrm{m^2/s})$	Q(kJ)	
	7.2(±1.98)	103.389	6.62(±1.30)	91.358	1.92(±0.844)	148.681	4.96(±2.61)	132.661	
a-axis	×10 ⁻⁵	(±4.34)	×10 ⁻⁵	(±4.04)	×10°	(±2.06)	×10 ⁻³	(±1.37)	Present
	9.96(±0.5)	105.020	7.02(±2.5)	91.877	1.72(±0.844)	148.431	2.22(±1.46)	128.987	Study
c-axis	×10 ⁻⁵	(±3.10)	×10 ⁻⁵	(±5.02)	×10°	(±1.25)	×10 ⁻³	(±1.48)	
Polycrystalline	3.23×10^{-7}	68.65	1.7×10 ⁻⁵	87.487	-	-	-	-	[8]

* Interdiffusion coefficient of Mg₅₁Zn₂₀ phase is 6.56 (\pm 0.88) $\times 10^{-14}$ m²/s at 603 K (330 °C) from the present study.



Fig. 5.1. (a) BSE image of interface microstructure of diffusion couple after 4 days of annealing at 593 K (320 °C), and (b) corresponding Zn concentration profile through the interface with the Matano plane location. (c) BSE image of interface microstructure of diffusion couple after 9 days of annealing at 603 K (330 °C) and (d) magnified image of the same interface near the Mg side showing the $Mg_{12}Zn_{13}$ and $Mg_{51}Zn_{20}$ phases.



(b)

Fig. 5.2. Intermetallic layer thickness vs. square root of diffusion annealing time at 573 K (300 °C) along the (a) a-axis, and (b) c-axis.


Fig. 5.3. Variation of the growth constant (k) of intermediate phases in the Mg-Zn system with temperature in comparison to previous experimental data [8, 9].



Fig. 5.4. Variation of the interdiffusion coefficient of intermediate phases in the Mg-Zn system with temperature in comparison to previous experimental data [8].



Fig. 5.5. Concentration profile of Zn inside hcp Mg single crystal after 4 days of annealing at 593 K (320 °C).



Fig. 5.6. Zn impurity diffusion coefficient in hcp Mg along its a- and c-axis with previous data derived from polycrystalline samples [4, 5]. For comparison, Mg self-diffusion coefficients [2] and Al diffusion coefficients in hcp Mg [10] are also reported. i = Zn, Al, Mg.

Chapter – 6

ThermodynamicModelingandDiffusionKineticExperiments of Binary Mg-Gd and Mg-Y Systems

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Prof. Y. B. Kang helped re-optimizing the Mg-Gd and Mg-Y pahse diagrams with present experimental data. Prof. T. K. Ha produced the Mg single crystals necessary for the experimental study. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision. All the Co-Authors provided valuable suggestions and comments and reviewed the manuscript before submission.

6.1 Abstract

Diffusion couple experiments for the Mg-Gd and Mg-Y systems were performed with Mg single crystals to investigate the anisotropic diffusion behavior of Gd and Y in hcp Mg at the temperatures between 703 and 803 K (430 and 530 °C). Diffusion coefficients for both Gd and Y along the basal plane of hcp Mg are about 1.3 times higher than those along the normal direction of the basal plane. The impurity diffusion coefficients of both Gd and Y in hcp Mg are lower than the self-diffusion of Mg and impurity diffusions of Al and Zn by about one order of magnitude. Growth constants and interdiffusion coefficients of the intermediate phases for both systems were determined. Accurate thermodynamic modeling of the Mg-Y and Mg-Gd systems were also carried out based on the phase diagram data obtained from the present diffusion couple experiments and available literature data.

Keywords: magnesium, anisotropic diffusion, phase diagram, thermodynamic modeling, rare earth.

6.2. Introduction

Mg-RE (Rare Earth) alloys have drawn industrial attention due to the effect of RE on the texture of Mg alloy. The role of RE elements on texture weakening is still being actively investigated, but the segregation of RE elements at grain boundaries and dislocations seems to provide a significant contribution to texture weakening [1-3]. The improved strength and creep resistance can be also obtained by formation of thermally stable precipitates containing RE elements [4-6]. The knowledge of thermodynamics and diffusion kinetics are important to understand and optimize the complex phase transformations and precipitation behavior in materials. Although there have been active thermodynamic and phase diagram studies on the Mg-RE alloy systems [7-12], no systematic diffusion kinetics studies have been performed for the Mg-RE systems so far.

Mg has an anisotropic hcp (hexagonal close packed) crystal structure (c/a lattice constant ratio = 1.6236). Shewmon [13] and Combronde et al. [14] were the first researchers to reveal the anisotropic self-diffusion of Mg using a radiotracer serial sectioning method. Mantina [15] later calculated the self-diffusion coefficients for Mg using first principles calculations. All their data show that the self-diffusion coefficient of Mg perpendicular to the c-axis (the basal plane) is higher than that along the c-axis (normal to the basal plane). Combronde et al. [16] also studied the anisotropic diffusion behavior of impurity elements (Ag, Cd, In, Sn and Sb) in Mg. Al and Zn are two common alloying elements in Mg alloys. The present authors [17, 18] investigated the anisotropic diffusions of Al and Zn using Mg single crystal diffusion couple experiments followed by a multiphase diffusion modeling. The impurity diffusions of Al and Zn are also about 1.3 times faster along the basal plane of Mg compared to that perpendicular to basal plane which is similar trend for anisotropic diffusions of most other impurity elements (Cd, In, Sn, Sb etc).

The main purpose of the present study is to determine the diffusion kinetics of the Mg-Gd and Mg-Y systems. Using Mg single crystal diffusion couple experiments, the anisotropic diffusion behaviors of Gd and Y in hcp Mg were studied and the interdiffusion coefficients of the intermetallics phases in both binary systems were determined. In addition, the phase diagram information obtained in the diffusion couple experiments were used for the re-optimization of the Mg-Gd and Mg-Y systems using the Calphad method.

6.3. Experimental

Magnesium single crystals were produced using a modified Bridgman furnace located at Gangneung-WonJu University, Korea. Mg bars were machined from high purity Mg ingots (99.99 wt. %, Magnesium Elektron) and inserted to a cone-shaped graphite mould. Unfortunately, the direction of each Mg single crystal cannot be controlled and hence the basal plane direction of produced single crystals is random. The cylindrical single crystals had a 10 mm diameter with maximum length of 15 cm. Direction of the basal plane in each single crystal produced by the Bridgman method was examined using a Bruker D8 XRD pole figure measurement and an Electron Backscattered Diffraction (EBSD) using Philips XL-30 Field Emission Scanning Electron Microscope (FE-SEM). Mg single crystals were cut very carefully using a Buehler IsoMet low speed diamond saw to avoid any surface deformation. A specially designed cutting jig was used to obtain sample Mg crystals with the surface parallel/perpendicular to the basal plane of Mg crystal. Polycrystalline pure Gd and Y (99.9 wt. %, HEFA Rare Earth Co. Ltd.) were sectioned into a small rectangle (15 mm x 15 mm x 10 mm) and then cut and ground into half-circular discs. These specimens were annealed at 723 K (450 °C) under a high purity Ar atmosphere to relieve any stress during the sample preparation and to obtain a large grain size (\sim 500 µm). The Mg, Gd and Y specimens were polished with 0.25 µm diamond suspension in an ethanol medium to obtain a flat surface and prevent surface oxidation. The orientation of each Mg single crystal specimen was confirmed by an XRD pole figure measurement before the diffusion experiments. Discs of Mg/Gd and Mg/Y were tied using a stainless steel clamp on the a- and c-axis of single crystal Mg.

To minimize the oxidation of the samples during the diffusion experiments, the samples were wrapped with Ta foil and high purity Ar gas (5 N) was flowed at 10 ml/min. The experiment was performed in a gas tight low temperature tube furnace. The furnace was equipped with two Ktype thermocouples, one for controlling the power and another one inside the furnace just above the diffusion couple sample for measuring the sample temperature. The annealing experiments were done at 703, 723 and 743 K (430, 450 and 470 °C) for 2 to 7 days for Mg-Gd system and 723, 743, 773 and 803 K (450, 470, 500 and 530 °C) for 2 to 5 days for Mg-Y system to make sure that all intermediate phases developed enough layers in the solid state. After the diffusion experiments, samples were taken out from the furnace and quickly quenched in ice cold water. The diffusion couple samples were then mounted into epoxy and cut perpendicular to the diffusion contact plane using a low speed diamond saw. They were then ground and polished with 0.05 µm colloidal silica suspension (OPS-Buehler). Each diffusion couple was examined using an optical microscope (Nikon-Clemex vision) to make sure the intermetallic layers at interface were well developed. Then, intermediate phases, Mg-, Gd- and Y-rich solid solution phases at the interface were examined using a Philips XL-30 FE-SEM and a JEOL 8900 Electron Probe Micro Analyzer (EPMA). The concentration profiles for Mg, Gd and Y through the interface were measured with EPMA-Wavelength Dispersive Spectroscopy (WDS). An accelerating voltage of 15 kV was used with a 20 nA beam current, a spot size about 1 μ m, and counting times of 20 seconds on peaks and 20 seconds on background. The detection limit of EPMA WDS was 0.05 wt. % for Mg, Gd and Y. The step size for line scans through the interface was 2 µm for all samples. Raw data was reduced with PRZ corrections using pure Mg, Gd and Y in the solid solution regions; however, intermetallic compounds (Mg₂₄Y₅ and Mg₃Gd) were also used for the correction within the intermediate phases.

The experimental diffusion couple data are given in supplementary (Appendix).

6.4. Thermodynamic modeling of the Mg-Gd and Mg-Y binary systems

Thermodynamic modeling of the Mg-Gd and Mg-Y binary systems were performed using the CALPHAD method. All thermodynamic calculations and optimizations for model parameters were performed with the FactSage thermochemical software [19]. The Gibbs free energies of all phases of pure Mg, Gd, and Y were taken from SGTE Unary database ver. 4.4 [20]. All model parameters used or optimized in the present study are listed in Table 6.1.

6.4.1. Thermodynamic models

6.4.1.1. Solid solution phases

Terminal solid solutions, hcp and bcc, and all intermetallic phases were modeled using the Compound Energy Formalism (CEF) considering appropriate sublattices structure. For example, Mg₂Gd exhibiting non-stoichiometry was modeled by assuming two-sublattices: $(Mg,Gd)_2(Gd, Mg)_1$. The Gibbs energy of the phase per formula in the CEF is then given by:

$$G = y'_{Mg} y''_{Gd} G_{Mg:Gd} + y'_{Mg} y''_{Mg} G_{Mg:Mg} + y'_{Gd} y''_{Gd} G_{Gd:Gd} + y'_{Gd} y''_{Mg} G_{Gd:Mg} + 2RT (y'_{Mg} \ln y'_{Mg} + y'_{Gd} \ln y'_{Gd}) + RT (y''_{Gd} \ln y''_{Gd} + y''_{Mg} \ln y''_{Mg}) + \sum_{i,j,k} y'_{i} y'_{j} y''_{k} L_{i,j:k} + \sum_{i,j,k} y'_{k} y''_{i} y''_{j} L_{k:i,j}$$
(6.1)

where y'_i and y''_j are the site fractions of component *i* and *j* on each sublattice, $G_{i:j}$ is the Gibbs energy of the end member $i_a j_b$. $L_{i,j:k}$ and $L_{k:i,j}$ are the interaction energies between components *i* and *j* on one sublattice when the other sublattice is occupied only by *k*. The terminal solutions, hcp and bcc, were treated as single sublattice solution. For the hcp phase where Gd(hcp) has a magnetic ordering ($T_{curie} = 293.4 \text{ K}$, $\beta = 3$), the magnetic contribution, as described by Inden, modified by Hillert and Jarl [21], was added to the Gibbs energy.

6.4.1.2. Liquid phase

The Gibbs energy of binary liquid phase was described using the Modified Quasichemical Model with pair approximations [22]. It was shown that the thermodynamic behavior of liquid Mg-RE system exhibiting chemical short-range ordering was well reproduced using the MQM [7, 8]. The following pair exchange reaction on neighboring lattice sites is considered for liquid Mg-RE solution.

$$(Mg-Mg) + (RE-RE) = 2(Mg-RE); \quad \Delta g_{MgRE}$$
(6.2)

where (i-j) represents the First-Nearest Neighbor (FNN) pair and Δg_{MgRE} is the Gibbs energy change for formation of two moles of (Mg-RE) pairs. Let n_i and n_{ij} be the number of moles of component *i* and (i-j) pairs, respectively. Let Z_{Mg} and Z_{RE} be the coordination numbers of Mg and RE, respectively, and they were assumed to vary with composition [22]. Then the Gibbs energy of the solution is given by:

$$G = \left(n_{\rm Mg}g_{\rm Mg}^{\circ} + n_{\rm RE}g_{\rm RE}^{\circ}\right) - T\Delta S^{config} + \left(n_{\rm MgRE}/2\right)\Delta g_{\rm MgRE}$$
(6.3)

where $g_{M_g}^{\circ}$ and g_{RE}° are the molar Gibbs energies of the pure liquid Mg and RE, and ΔS^{config} is the configurational entropy of mixing given by randomly distributing the (Mg–Mg), (RE–RE), and (Mg–RE) pairs in the one-dimensional Ising approximation given by Pelton et al.[22]. The model parameter Δg_{MgRE} can be expanded as a polynomial of pair fractions (X_{ij}):

$$\Delta g_{\text{MgRE}} = \Delta g_{\text{MgRE}}^{o} + \sum_{i \ge 1} g_{\text{MgRE}}^{i0} X_{\text{MgMg}}^{i} + \sum_{j \ge 1} g_{\text{MgRE}}^{0j} X_{\text{RERE}}^{j}$$
(6.4)

The equilibrium pair distribution can be calculated by the condition:

$$(\partial G/\partial n_{\rm MgRE})_{n_{\rm Mg}, n_{\rm RE}} = 0 \tag{6.5}$$

Detailed mathematical descriptions (quasichemical approximation of the configurational entropy, composition dependent coordination number, *etc.*) of the model can be found elsewhere [22].

6.4.2. Thermodynamic optimization

6.4.2.1. The Mg-Gd system

Experimental investigations up to 1986 have been reviewed by Nayeb-Hashemi and Clark [23]. Thermodynamic modeling of this system has been performed several times [9, 11, 24, 25]. There are four intermetallic phases: Mg₃Gd, Mg₃Gd, Mg₂Gd and MgGd. Most of the previous modeling works assumed intermetallic phases as stoichiometric compounds. Caciamani et al. [25] treated Mg₂Gd and MgGd phases as non-stoichiometric solid solutions and Guo et al. [11] assumed the MgGd solution in their modelings. However, no experimental evidence of non-stoichiometry was available at the time of their modeling. The most recent thermodynamic assessment by Hampl et al. [9] assumed all the intermetallic phases as stoichiometric compounds. In the present modeling, all the intermetallic phases were treated as non-stoichiometric solid solution phases based on the present experimental results. While all previous modeling works used a random mixing model [9, 11, 24, 25] for liquid phase, the present study used MQM to describe the short range ordering in liquid.

Optimized phase diagram of the Mg-Gd system along with experimental data is presented in Fig. 6.1. There are four intermetallic phases (Mg₅Gd, Mg₃Gd, Mg₂Gd and MgGd) as well as two terminal solutions (hcp and bcc). Liquidus and invariant reactions of the system were well characterized by Manfrinetti and Gschnieidner [26] and Rokhlin and Nikitina [27]. The solubility

of Gd in the $(Mg)_{hep}$ measured in this study is in good agreement with those reported earlier [9, 27]. Solubility of Mg in the $(Gd)_{hep}$ measured in this study is also in good agreement with those reported earlier [28]. Non-stoichiometries of Mg₅Gd, Mg₃Gd, and Mg₂Gd were observed in the present diffusion couple experiment, which were well described in the present study using two sublattice CEF. A eutectic reaction at Mg-rich side (L \rightarrow (Mg)_{hep} + Mg₅Gd) was calculated at 822 K (549°C), which is very close to the experimental values of 815 ~ 821 K (542 ~ 548 °C) [9, 26, 29, 30]. The calculated liquidus of hcp Mg was slightly lower than experimental data [26, 27]. However, attempts to reproduce the experimentally determined liquidus data induced deviations in the eutectic temperature.

Thermodynamic properties of solid phases were simultaneously optimized based on the both calorimetric enthalpy data and Mg vapor pressure data for the equilibration of two adjacent solid phases, as shown in Fig. 6.2. Fig. 6.2 (a) shows the enthalpy of formation of intermetallic phases. There is only one calorimetric measurement (only for the MgGd phase) [31]. The first principles calculations by Tao et al. [32] are much less negative than the experimental point. Enthalpies of solid phases derived from vapor pressure measurement [33] were more exothermic than the calorimetric. The Mg vapor pressure data of Pahlman and Smith [33] and Ogren et al. [34] were compared in Fig. 6.2 (b). Although the two data sets were reported from the same laboratory there are large discrepancies in the results. The slope of experimental data in Fig. 6.2(b) is determined by the enthalpy difference between equilibrium phases. Recent systematic thermodynamic modeling of Mg-RE (RE = La, Ce, Pr, Nd, Sm) system [8] showed that the vapor pressure data of the same authors are less consistent with other experimental data such as phase diagram and enthalpy of formation data. One of possible reasons of the discrepancy is due to the usage of stoichiometric starting materials. Therefore the non-stoichiometry of intermetallic phases could not be fully developed during the experiment. Therefore, less weight was given to these data but the present thermodynamic modeling can still reasonably reproduce the vapor pressures of Mg. The optimized enthalpy of mixing of the Mg-Gd binary liquid at 1000 K (727 °C) is plotted in Fig. 6.2 (c). Previous thermodynamic modelings [9, 11, 25] except that by Cacciamani et al. [24] shows a minimum in the enthalpy of mixing near $X_{Gd} = 1/3$ as in the present study. The positive deviation by Hampl et al. [9] in Gd-rich region seems to be

erroneous. The minimum enthalpy of mixing of the liquid Mg-Gd phase is about -9 kJ/g-atom which is in the same range as other heavy Mg-RE systems.

6.4.2.2. The Mg-Y system

The literature of the Mg-Y system up to 1983 has been critically reviewed by Nayeb-Hashemi and Clark [35]. Kang *et al.* [7] performed the thermodynamic modeling of this system after reviewing the literature data published until 2003. Many other studies [11, 36-39] also performed the thermodynamic assessments of this system. Recently, Zhao et al. [40] and Bermudez et al. [41] reported the significant non-stoichiometries of intermetallic phases from their diffusion couple data in the temperature range between 623 and 823 K (350 and 550°C). Similar results were obtained in the present experiments. As these results are significantly different from the thermodynamic modeling results so far, new thermodynamic modeling of the Mg-Y system is needed.

Optimized phase diagram of the Mg-Y system along with available experimental data is shown in Fig. 6.3. There are three intermetallic phases: Mg₂₄Y₅, Mg₂Y, and MgY. The liquidus and solidus of the system was determined by the Gibson and Carlson [42] DTA. The sub-solidus equilibria were examined by Smith et al. [43] using Mg vapor pressure and calorimetry, and Gibson and Carlson [42] and Flandorfer et al. [44] using XRD after equilibration. The present experimental data show the solid solutions of Mg₂₄Y₅ and Mg₂Y bend significantly toward Mg side, which are well consistent with the experimental data by Bermudez et al. [41]. Noticeable solubility of Mg in Y at temperature below 773 K (500 °C) was determined for the first time in this study. The present experimental solubility of Y in Mg is good agreement with the results of Zhao et al. [40]. The liquidus and all the recent experimental data in solid state are well reproduced in the present modeling.

Calculated enthalpy of formation at 298 K, partial pressure of Mg in the solid state and enthalpy of mixing in liquid phase are shown in Fig. 6.4. All the experimental data [43, 45] were simultaneously optimized with phase diagram data in Fig. 6.3. Among all the modelings, only Ran et al. [36] shows the unlikely positive deviation in enthalpy of mixing. The liquid model

parameters were only slightly changed from the previous modeling by Kang et al. [7]. The optimized enthalpy of mixing of liquid phase shows the minimum of about -8 kJ/g-atom near $X_Y = 1/3$.

6.5. Diffusion kinetics of Mg-Gd and Mg-Y systems

SEM Backscattered Electron (BSE) image at the interface of Mg-Gd diffusion couple sample annealed at 743 K (470 °C) for 2 days are shown in Fig. 6.5 (a) and (b). Five different intermetallic layers were found at the interface. The BSE image and WDS line scan (Fig. 6.6 (a)) confirmed the existence of Mg₅Gd, Mg₃Gd, Mg₂Gd, and MgGd solution phases. There is one more phase next to Gd, but WDS was unable to determine the exact composition of this layer (Fig. 6.5 (b)) due to its small thickness (less than a micron). Our best analysis tells it is close to Mg₄Gd₆. Because the composition was not well determined and the thermal stability of this phase is not known yet, it was not taken into account in the thermodynamic modeling. BSE images of the Mg-Y diffusion couple sample annealed at 773 K (500 °C) for 2 days is shown in Fig. 6.5 (c) and (d) and the WDS line scan is presented in Fig. 6.6 (b). Three intermetallics, Mg₂₄Y₅, Mg₂Y, and MgY, were observed in the Mg-Y system. The newly optimized phase diagrams in Figs. 6.1 and 6.3 considered the present experimental data. Both Gd and Y have atomic radii of 180 pm whereas the atomic radius of Mg is 160 pm, which can make it easier for Mg to diffuse into Gd and Y. As a result, most of the intermetallic phases formed toward Gd and Y side of the diffusion couples. The experimental results (thickness of the intermetallic layers with annealing temperature and time) are summarized in the supplementary (Appendix) of the present study.

6.5.1. Growth kinetics and interdiffusion in intermetallic phases

Growth kinetics for the intermetallic phases of both the Mg-Gd and Mg-Y systems were evaluated by examining all the diffusion couple samples. Nucleation time for the intermetallic phases was assumed negligible compared with the present annealing time. This is a key assumption to calculate diffusion kinetics properly in diffusion couple experiment. To prove the validity of this assumption, layer thickness against square root of time was plotted in Fig. 6.7. Linear fit of the experimental data for each intermetallic layer intersects through the origin, which proves our assumption is valid. A parabolic growth constant based on the diffusion controlled growth can be determined from the results using the following equation:

$$x = k\sqrt{t} \tag{6.6}$$

where *x* is the thickness of intermetallic layer, *t* is annealing time and *k* is growth constant. An Arrhenius relationship can be applied for the growth constant *k*:

$$k = k_0 \exp(-Q/RT) \tag{6.7}$$

where k_o (m/s^{0.5}) is the pre-exponential factor, *R* (J/mol-K) the gas constant, *Q* (J/mol) the activation energy and *T* the annealing temperature in Kelvin. Growth constants of intermetallic phases in both Mg-Gd and Mg-Y systems were found to be independent of the orientation of the hcp Mg crystal. Growth constants and activation energies for Mg-Gd intermetallic phases and Mg-Y intermetallic phases calculated from the present experiments are listed in Table 6.2. The growth constants of Mg₂₄Y₅ and Mg₂Y phases are in good agreement with the previous results by Zhao et al. [40] and Bermudez et al. [41]. There are no studies for the growth constants of MgY phase and any Mg-Gd intermetallic phases to compare with the present results.

Interdiffusion coefficient of intermetallic phases in binary alloys can be calculated using the famous Heumann-Matano method [46]. This method can be applied for the intermediate phase that has a linear concentration profile throughout the entire phase:

$$\tilde{D}_{i} = -\frac{1}{2t} \frac{W_{i}}{\Delta C_{i}} \int_{0}^{c_{i}^{1/2}} x dC_{i}$$
(6.8)

where D_i and C_i are the interdiffusion coefficient (m²/s) and the concentration of solute of *i* phase, respectively, *x* the distance from the Matano interface (m), *t* the diffusion time (sec), w_i the layer thickness of *i* phase (m), ΔC_i the concentration difference of solute between both ends of *i* phase, and $C_i^{1/2}$ is the middle solute composition of *i* phase.

For the Mg-Gd system, the interdiffusion coefficients of Mg₅Gd, Mg₃Gd, and Mg₂Gd phases were calculated using Eq. (6.8), whereas MgGd phase is too thin to accurately determine the interdiffusion coefficient using the same method and thus it was calculated using a multiphase diffusion model that is discussed in section 4.2.1. Strictly speaking, the interdiffusion coefficient of Mg₂Y cannot be accurately calculated by the Heumann-Matano method because the variation of composition with distance deviates largely from linearity as can be seen in Fig. 6.6 (b), but we simply adopted this method without further complication. In the Mg-Y system, Mg₂₄Y₅ and Mg₂Y phases have large enough thickness and inhomogeneity to calculate interdiffusion coefficient using Eq. (6.8), whereas interdiffusion coefficient of MgY phase was calculated using a multiphase diffusion model. All the interdiffusion coefficients for Mg-Gd and Mg-Y systems are listed in Table 6.3.

6.5.2. Anisotropic impurity diffusion coefficient of Gd and Y in hcp Mg

One of the prime interests of the present study is to find the anisotropic diffusion coefficients of Gd and Y along the a- and c-axis of hcp Mg crystal. Concentration profiles of Gd and Y were acquired in the hcp Mg solid solution region by WDS line scanning with a step size of 2 μ m.

Several line scans were taken for each sample to confirm the reproducibility of the data. For example, concentration profiles of Gd in hcp Mg along the a- and c-axis at 743 K (470 °C) after 2 days of annealing are presented in Fig. 6.8 (a), the same for Y profiles at 773 K (500 °C) after 2 days of annealing are presented in Fig. 6.8 (b). Concentration profile depths of both Gd and Y along the a-axis of Mg are slightly longer than those along the c-axis of Mg. That is, the diffusivity of Gd and Y are slightly faster along the basal plane of Mg than perpendicular to the basal plane.

Diffusion coefficients of Gd and Y in hcp Mg along the a- and c-axis could be determined either by a multiphase diffusion simulation or by an analytical method.

6.5.2.1. A multiphase diffusion simulation approach

A multiphase diffusion model was developed to find the diffusion coefficient of solute in hcp Mg. The diffusion coefficient in hcp Mg could be determined by reproducing the concentration profile of solute through the interface for each experimental diffusion couple sample. This model was already applied to Mg-Al and Mg-Zn diffusion couple experiments to calculate the diffusion coefficients of Al and Zn in Mg depending on the orientations of hcp Mg.

Diffusion modeling is done by solving Fick's second law:

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x} \left(D_m^i \frac{\partial C_m}{\partial x} \right) \tag{6.9}$$

where C_m is the concentration of component *m*, *t* the time, *x* the distance, and D_m^i (m/s²) the diffusion coefficient for component *m* in *i* phase. For an intermetallic phase, the interdiffusion coefficient is used in Eq. (6.9). Composition dependent diffusion coefficient (D_m^i) can be expressed using mobility in combination with the thermodynamic chemical potential (μ) [47]. For example, D_m^{hcp-Mg} can be expressed as:

$$D_m^{hcp-Mg} = D_{mm}^{hcp-Mg} - D_{Mgm}^{hcp-Mg}$$

$$\tag{6.10}$$

$$D_{mm}^{hcp-Mg} = y_m y_{Mg} \Omega_m^{hcp-Mg} \frac{d\mu_m^{hcp-Mg}}{dy_m}$$
(6.11)

$$D_{Mgm}^{hcp-Mg} = y_m y_{Mg} \Omega_{Mg}^{hcp-Mg} \frac{d\mu_{Mg}^{hcp-Mg}}{dy_m}$$
(6.12)

where y_{Mg} and y_m are the mole fraction or site fraction of Mg and m (m = Gd or Y), respectively. In the present study, mole fraction and site fractions are identical. Ω_{Mg}^{hcp-Mg} and Ω_{m}^{hcp-Mg} are the mobility of Mg and m in hcp Mg, respectively. μ_{Mg}^{hcp-Mg} and μ_{m}^{hcp-Mg} are the chemical potentials of Mg and m in hcp Mg, respectively, which are obtained from the present thermodynamic modeling discussed in section 3.

The diffusion equation was solved using a finite difference method (FDM) coded in FORTRAN language to complete the multiphase diffusion calculations. In solving multiphase diffusion, the most critical part is the moving boundary problem (also known as Stefan problem) at the interface of the phases. The Murray-Landis transformation [48] has been applied by many researchers [49-51] to moving boundary problems occurring in multiphase diffusion calculations. In the present study, the moving boundary problem was also treated by the Murray-Landis

transformation [47] using an explicit method. The details of the multiphase diffusion simulation can be found elsewhere [17, 18, 52].

In the multiphase diffusion simulation, Ω_{Mg}^{hcp-Mg} ($\Omega_{Mg}^{hcp-Mg} = D_{Mg}^{hcp-Mg}$ /RT) depending on the orientation of hcp Mg solution was derived from the self-diffusion coefficients of Mg determined by Combronde et al. [14]: $D_{\perp Mg}^{hcp-Mg} = 1.75 \times 10^{-4} \exp(-137979/\text{RT})$ and $D_{II Mg}^{hcp-Mg} = 1.78 \times 10^{-4} \exp(-137979/\text{RT})$ 138943/RT). The Ω_{Y}^{hcp-Y} ($\Omega_{Y}^{hcp-Y} = D_{Y}^{hcp-Y}/RT$) in hcp Y solution was derived from the self-diffusion coefficients of Y determined by Gornyi et al. [53]: $D_{\perp Y}^{hcp-Y} = 5.2 \times 10^{-3} \exp(-252054/\text{RT})$ and $D_{II Y}^{hcp-Y}$ = $8.2 \times 10^{-5} \exp(-280060/RT)$. There was no mobility or diffusivity data found for Mg diffusion in Y in the literature and solubility of Mg in Y was also found to be small from the present WDS line scan. The mobility of Mg in hcp Y ($\Omega_{M_g}^{hcp-Y}$) was assumed to be two order of magnitude lower than self-diffusivity of Mg, $\Omega_{Mg}^{hcp-Y} = 1.75 \times 10^{-6} / \text{RT} \exp(-137979/\text{RT})$, which could roughly reproduce the concentration profile in Y phase. No diffusivity or mobility data for Gd are found in literature. Therefore, it was assumed that Gd has the same mobility values as Y because Y and Gd show very similar physical and chemical properties. The interdiffusion coefficient for each intermetallic phase was taken from the present measurement discussed in section 4.1 (Table 6.3). In the present simulation, the starting thickness of each intermediate phase was set to be 0.1 µm. The interface boundary composition for hcp phase and intermediate phases were taken from the experimental WDS concentration profile. In the simulation, the anisotropic mobilities of Y and Gd in hcp Mg could be determined by reproducing the concentration profiles of Y and Gd in hcp Mg. The interdiffusion coefficients of MgY and MgGd phases were also determined to reproduce their layer thicknesses from the diffusion couple experiments.

6.5.2.2 An analytical approach

A Gaussian solution for Fick's diffusion equation (Eq. (6.13)) for a constant diffusivity and one dimensional diffusion under very dilute region is given by Jost [54]:

$$C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt})$$
(6.13)

where *C* is the concentration, *D* is the diffusion coefficient, *M* is the number of particles diffusing per unit area, *x* is the diffusion depth and *t* is the diffusion annealing time. The diffusion coefficient can be calculated by plotting the natural logarithm of solute concentration against the square of diffusion depth (x^2) obtained from WDS line scans in very dilute region (less than 1 at. % of solute in hcp Mg). As can be seen in Fig. 6.9, the linear slope can be found in the plot for all samples and the slope is corresponding to -1/4Dt according to Eq. (6.13). For a known diffusion time (annealing time in the experiment) *t*, the diffusion coefficient *D* can be calculated from this plot. This diffusion coefficient *D* is typically termed as tracer or impurity diffusion coefficient.

6.5.2.3. Anisotropic impurity diffusion coefficient of Gd and Y in hcp Mg

The optimized mobilities of Gd and Y in hcp Mg along the a- and c-axis of Mg crystal from the present study are:

$$\Omega_{\perp Gd}^{hcp-Mg} = 7.53 \times 10^{-14} \exp(-73048/\text{RT})$$
(6.14)

$$\Omega_{II Gd}^{hep-Mg} = 1.06 \times 10^{-13} \exp(-75466/\text{RT})$$
(6.15)

$$\Omega_{\perp Y}^{hcp-Mg} = 1.62 \times 10^{-12} \exp(-91519/\text{RT})$$
(6.16)

 $\Omega_{\mu \gamma}^{hcp-Mg} = 1.79 \times 10^{-12} \exp(-94094/\text{RT})$ (6.17)

The impurity diffusion coefficients of Gd and Y in hcp Mg can be calculated by extrapolating the interdiffusion coefficients of hcp Mg solid solution (or diffusion coefficient of Gd and Y in hcp Mg) very carefully to zero amount of Gd and Y in hcp Mg solid solution. The obtained anisotropic impurity diffusion coefficients for Gd and Y in hcp Mg are:

$$D_{+Gd}^{hcp-Mg} = 1.27 \times 10^{-9} \exp(-79268/\text{RT})$$
(6.18)

$$D_{\mu Gd}^{hcp-Mg} = 1.79 \times 10^{-9} \exp(-81687/RT)$$
(6.19)

$$D_{\perp Y}^{hcp-Mg} = 2.79 \times 10^{-8} \exp(-97852/\text{RT})$$
(6.20)

$$D_{\mu \gamma}^{hcp-Mg} = 3.21 \times 10^{-8} \exp(-99127/\text{RT})$$
(6.21)

These values are very similar to those obtained from analytical method explained in 4.2.2. The impurity diffusion coefficients of Gd and Y in hcp Mg are plotted in Fig. 6.10. For both Gd and Y, the impurity diffusion coefficients along the a-axis of hcp Mg is slightly higher than along the c-axis of hcp Mg and the anisotropy of diffusivity becomes smaller with increasing temperature: D_{\perp}/D_{\parallel} of Gd in hcp Mg = 1.23 at 703 K (430 °C) and 1.04 at 743 K (470 °C) and D_{\perp}/D_{\parallel} of Y in hcp Mg = 1.32 at 723 K (450 °C) and 1.08 at 803 K (530 °C). The similar diffusion behavior was reported by the present authors for Al and Zn in hcp Mg using Mg single crystal diffusion couple experiments [17, 18]: D_{\perp}/D_{\parallel} of Al in hcp Mg = 1.33 at 638 K (365 °C) and 1.18 at 693 K (420 °C), and D_{\perp}/D_{\parallel} of Zn in hcp Mg = 1.23 at 553 K (280 °C) and 1.17 at 603 K (330 °C). The temperature dependence of the anisotropic diffusivities of Gd and Y can also tell that there is possibility that the diffusion along the c-axis of hcp Mg may become faster than that along the a-axis at high temperature (T > 823 K), but this should be further investigated.

Impurity diffusion coefficients for Y and Gd in hcp Mg are compared with those of Al and Zn [17, 18] in Fig. 6.11. The self-diffusion coefficient [14] of Mg is also plotted (Fig. 6.11) for

comparison. The diffusion coefficients of Y and Gd are similar to each other and are almost one order of magnitude lower than those of Al and Zn. Low diffusion coefficients of Gd and Y (Rare Earth Elements: REE) can be expected due to large atomic size of Gd and Y compared to those of Mg, Al and Zn. However, this study is the first to report accurate diffusion coefficients of REE in Mg. It should be also noted that the activation energies (a slope of diffusion coefficients in Fig. 6.11) of Gd and Y are smaller than those of Al and Zn. It is hard to explain why REE can have lower activation than Al or Zn at this stage. The difference in the diffusivities of conventional solutes like Al and Zn and REE like Gd and Y becomes smaller at lower temperature but larger at higher temperature.

Recent studies focusing on Mg-RE alloys show that REE can play an important role in the recrystallization behavior of Mg and randomization of texture during deformation or postannealing process. One of conclusions is that the REE's solute dragging effect of grain boundary during annealing can weaken the orientation of textures [55]. This can be explained by low diffusion coefficients of REE compared to Mg and other conventional solutes as shown in Fig. 6.11. In addition, such a slow diffusion speed of REE in Mg can control the precipitation behavior of RE containing intermetallics phases such as Mg_xRE_y, Al_xRE_y, Zn_xRE_y, Mg_xZn_yRE_z, Mg_xAl_yRE_z. That is, instead of forming large precipitates, high number density of small RE containing precipitates can be formed during annealing and ageing process.

There is no systematic study for REE diffusion in Mg until now. Although it is a bit dangerous to generalize the present results in all REEs, it could be said that most REEs could have similar diffusivity values, about one order of magnitude lower than those of Mg, Al and Zn, considering the similarity in physico-chemical properties within REE group.

6.6. Summary

Diffusion couple experiments for the binary Mg-Gd and Mg-Y systems were performed using Mg single crystals in the temperature range between 703 and 803 K (430 and 530 °C). The equilibrium phase diagram information for the two binary systems were obtained. The inhomogeneity ranges of several intermetallic phases in the Mg-Gd system were determined for Page | 139

the first time, and the existence of a new Mg₄Gd₆ intermetallic phase was reported. The discrepancy in the phase diagram information for the Mg-Y system was resolved. Based on the present experimental data and literature data, accurate thermodynamic modeling of the Mg-Gd and Mg-Y systems were carried out using the CALPHAD technique.

The anisotropic diffusion behaviors of Gd and Y in hcp Mg were determined for the first time. The anisotropy in diffusion coefficient of Gd in hcp Mg is $D\perp/D_{\parallel} = 1.23$ at 703 K (430 °C) and that of Y is $D\perp/D_{\parallel} = 1.32$ at 723 K (450 °C), which decrease with increasing temperature. It should be noted that the impurity diffusion coefficients of Gd and Y are similar each other but about one order of magnitude lower than the impurity diffusions of Al and Zn and the self-diffusion of Mg. The diffusion activation energies of Gd and Y are also significantly lower than those of Al and Zn. The growth kinetics and interdiffusion coefficients of Mg-Gd and Mg-Y intermetallic phases were also determined.

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Liquid	(Mg,Gd) and (Mg,Y)
$Z_{\rm MgMg}^{\rm Mg} = Z_{\rm MgMg}$	$I_{Gd} = Z_{YY}^{Y} = Z_{MgGd}^{Gd} = Z_{MgY}^{Y} = 6, Z_{MgGd}^{Mg} = Z_{MgY}^{Mg} = 3$
$\Delta g_{ m MgGd}$	$-12970.4 + 3.7656T - 12133.6X^2_{MgMg} + 1255.2X_{GdGd}$
$\Delta g_{ m MgY}$	$-12761.2 + 4.184T + (-8368 + 5.7321T)X^{2}_{MgMg} + 2092X^{2}_{YY}$
hcp	(Mg,Gd) ₁ (Va) and (Mg,Y) ₁ (Va)
L _{Gd,Mg:Va}	$-24267.2 + 8.368T + 18828(y'_{\rm Gd} - y'_{\rm Mg}) - 5020.8(y'_{\rm Gd} - y'_{\rm Mg})^2$
$L_{\mathrm{Mg,Y:,Va}}$	$-25104 + 13.598T - 6066.8(y'_{Mg} - y'_{Y})$
$T^{\rm fcc}$	293.4y' _{Gd}
β^{fcc}	$3y'_{Gd}$
bcc	(Mg,Gd) ₁ (Va) and (Mg,Y) ₁ (Va)
L _{Gd,Mg:Va}	$-25522.4 + 7.9496T + 5439.2(y'_{Gd} - y'_{Mg})$
$L_{\rm Mg,Y:,Va}$	$-43932 + 20.92T - 6276(y'_{Mg} - y'_{Y})$
Mg ₂ Y	$(Mg,Y)_2(Y,Mg)_1$
G	$_{g:Y} \qquad 2GHSERMG + GHSERYY - 35732.5 + 5.7845T$
G_{I}	$_{g:Mg}$ 3GHSERMG + 5586.209 - 2.5 <i>T</i>
(3GHSERYY + 30000
G	$Mg \qquad \qquad GHSERMG + 2GHSERYY + 67548.96 - 5.3448T$
$L_{Mg:,Mg,Y} = L$	_{,Mg,Y} -25104
Mg_2Gd	$(Mg,Gd)_2(Gd,Mg)_1$
G_{1}	$_{g:Gd}$ 2GHSERMG + GHSERGD -12189 + 4.65T
G_{I}	3GHSERMG + 5434.99 - 4 T
G	3GHSERGD + 1000 + 3 T
G	GHSERMG + 2GHSERGD + 2000
$L_{Mg,Gd:Mg} = L_{Mg,Gd:Mg}$	-25104 + 20.92T
$L_{\mathrm{Mg:,Mg,Gd}} = 1$	-41840 + 20.92T
Mg ₂₄ Y ₅	$(Mg,Y)_{10}(Mg)_{24}(Mg)_{24}$
G_{Mg}	Ag:Mg 58GHSERMG + 42000 - 30.0T
$G_{ m Y}$	48GHSERMG + 10GHSERYY -128643.54 + 42.7 <i>T</i>
MgGd, Mg	(Mg) ₁ (Mg,Gd) ₁ and (Mg) ₁ (Mg,Y) ₁
G_{I}	2GHSERMG + 2500

Table 6.1. Optimized thermodynamic model parameters in the present study (J/mol).

$G_{ m Mg}$	g:Gd	GHSERMG + GHSERGD -7170.172 + 1.748820 <i>T</i>
$G_{ m M}$	g:Y	GHSERMG + GHSERYY -6938.583 + 1.448375 <i>T</i>
Mg ₃ Gd		$(Mg,Gd)_3(Gd,Mg)_1$
$G_{ m Mg}$	g:Gd	3GHSERMG + GHSERGD - $15296 + 5.4T$
$G_{ m Mg}$:Mg	4GHSERMG + 500
$G_{ m Gd}$	l:Gd	4GHSERGD + 3000 + 1T
$G_{ m Gd}$:Mg	GHSERMG + 3GHSERGD + 2000
$L_{\text{Mg:,Mg,Gd}} = L_{\text{G}}$	Gd:,Mg,Gd	-4184
Mg ₅ Gd		$(Mg)_5(Gd,Mg)_1$
$G_{ m Mg}$	g:Gd	5GHSERMG + GHSERGD - 21200 + 9.400488 <i>T</i>
$G_{ m Mg}$::Mg	6GHSERMG + 3500

GHSERGD, GHSERMG, GHSERYY are standard Gibbs free energies of pure Gd, Mg, Y at 298 K, 1 bar (hcp_A3), respectively, and their values are given in Ref. [20]. Gibbs free energies of pure Gd, Mg, and Y for bcc and liquid phases were also taken from Ref. [20].

	orientation (diffusion direction) of Mg single crystal			Ma polyerystalling			
Intermetallics	a-axis		c-axis		wig porycrystannie		
	k_{0}^{2} (m ² /s)	Q (kJ/mol)	k_{0}^{2} (m ² /s)	Q (kJ/mol)	k_{0}^{2} (m ² /s)	Q (kJ/mol)	
Mg5Gd	4.44×10^{-8}	97.21	4.34×10^{-8}	97.27			
Mg ₃ Gd	3.78×10^{-7}	98.43	3.34×10^{-7}	97.75			
Mg ₂ Gd	4.43×10^{-7}	104.15	3.19×10^{-7}	102.31			
MgGd	4.94×10^{-12}	80.26	6.78×10^{-12}	82.42			
Mg_4Gd_6	1.36×10^{-10}	109.22	1.54×10^{-10}	110.22			
Mga V.	6.39×10^{-10}	62.57	5.65×10^{-10}	63.43	3.58×10^{-10}	61.59*	
1 v1g 24 1 5						8.84×10 ⁻⁹	83.6+
	4.02×10^{-10} 71.24	71.24	4.14×10 ⁻¹⁰	70.53	1.93×10^{-10}	60.84*	
Mg ₂ Y					4.89×10^{-10}	77.3+	
MgY	2.02×10^{-8}	136.34	3.36×10^{-8}	138.78			

Table 6.2. Growth constants of intermetallic phases in the Mg-Gd and Mg-Y systems determined from the present study in comparison with previous literature data.

* Zhao et al. [40] and ⁺Bermudez et al. [41]

Table 6.3. Interdiffusion coefficients of intermetallic phases in the Mg-Gd and Mg-Y systems determined from the present study.

	orientation (diffusion direction) of Mg single crystal					
Intermetallics	a-a	xis	c-axis			
	$D_{\rm o}({\rm m^2/s})$	Q (kJ/mol)	$D_{\rm o}({\rm m^2/s})$	Q (kJ/mol)		
Mg ₅ Gd	2.78×10^{-5}	102.51	3.08×10^{-5}	103.95		
Mg ₃ Gd	3.96 × 10 ⁻²	152.85	8.28×10 ⁻²	157.02		
Mg ₂ Gd	3.07×10^{-6}	98.81	2.46×10^{-6}	97.28		
MgGd	1.05×10^{-6}	100.04	1.62×10^{-6}	102.76		
Mg ₂₄ Y ₅	5.43×10 ⁻⁸	78.50	6.48×10 ⁻⁸	80.67		
Mg ₂ Y	3.23×10^{-8}	85.96	3.81×10 ⁻⁸	87.28		
MgY	5.38×10^{-7}	109.67	4.96×10^{-7}	108.53		



Fig. 6.1. Calculated phase diagram of the Mg-Gd system in the present study with experimental data.



Fig. 6.2. Calculated thermodynamic properties of the Mg-Gd system with experimental data: (a) enthalpy of formation of intermetallic phases, (b) vapor pressure of Mg in the solid state, and (c) enthalpy of mixing of liquid phase.



Fig. 6.3. Calculated phase diagram of the Mg-Y system in the present study with experimental data.



Fig. 6.4. Calculated thermodynamic properties of the Mg-Y system with experimental data: (a) enthalpy of formation of intermetallic phases, (b) vapor pressure of Mg in the solid state, and (c) enthalpy of mixing of liquid phase.



Fig. 6.5. SEM BSE images of diffusion couple interface: (a) Overview of the Mg-Gd diffusion couple after 2 days annealing at 743 K (470 °C) and (b) magnified view of Gd side at the interface of the Mg-Gd diffusion couple. (c) Overview of the Mg-Y diffusion couple after 2 days annealing at 773 K (500 °C) and (d) magnified view of Y side at the interface of the Mg-Y diffusion.


Fig. 6.6. Solute concentration profile (WDS line scan) through the diffusion interface: (a) Gd profile at Mg-Gd diffusion couple interface after 2 days annealing at 743 K (470 °C), and (b) Y profile at Mg-Y diffusion couple interface after 2 days annealing at 773 K (500 °C).



Fig. 6.7. Thickness of intermetallic layer vs. square root of diffusion annealing time: (a), (b) Mg-Gd intermetallic phases annealing at 743 K (470 °C), and (c), (d) Mg-Y intermetallic phases annealing at 773 K (500 °C).



Fig. 6.8. Experimental EPMA-WDS solute concentration profiles in hcp Mg single crystals depending on the orientation of Mg crystals. (a) Concentration of Gd after 2 days at 743 K (470 °C), and (b) the concentration of Y after 2 days at 773 K (500 °C).



Fig. 6.9. Logarithm of solute concentration profile against square of depth (distance) at the dilute solute concentration region in hcp Mg single crystals. (a) Gd diffused after 2 days at 743 K (470 °C) and (b) Y diffused after for 2 days at 773 K (500 °C). Dotted and solid lines are regressed lines for a-axis and c-axis data, respectively.



Fig. 6.10. Impurity diffusion coefficients of (a) Gd and (b) Y in hcp Mg along the a- and c-axis directions of hcp Mg, determined from the present diffusion couple experimental data using diffusion simulation and analytical method.



Fig. 6.11. Comparison of the anisotropic impurity diffusion coefficients of Gd and Y in hcp Mg with those of Al and Zn [17, 18] and Mg self-diffusion coefficients [14].

Chapter – 7 Grain boundary diffusion of Al in Mg

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Mr. N. Brodusch helped with the microanalysis by CFE-SEM. Prof. R. Gauvin provided with a new technique for quantitative analysis of Al with CFE-SEM. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision. All the Co-Authors reviewed the manuscript before submission.

7.1 Abstract

Grain boundary diffusion of Al in polycrystalline Mg was measured from diffusion couple experiments between 603 and 693 K with a high resolution CFE-SEM EDS microanalysis. Grain boundary diffusion of Al is found to increase with increasing misorientation between adjacent Mg grains, and grain boundary diffusion coefficients of Al can be two orders of magnitude faster than volume diffusion of Al in hcp Mg. The difference between grain boundary and volume diffusion of Al becomes larger at lower temperatures.

Keywords: grain boundary diffusion, magnesium alloys, aluminium, diffusion couple.

7.2. Introduction

Mg-Al based alloys are the most common magnesium alloy for industrial applications. To understand the thermochemical reactions at elevated temperature, the knowledge of thermodynamics and diffusion kinetics is critical. Thermodynamics of the binary Mg-Al system have been well investigated. Recently, the present authors [1] reported the anisotropic diffusion behavior of Al in hcp Mg (impurity diffusion of Al in bulk volume) using Mg single crystal diffusion experiments. According to the experimental data, the diffusion of Al through the basal plane of Mg is slightly faster than perpendicular to the basal plane: $D\perp/D_{\parallel}$ of Al in hcp Mg = 1.33 at 638 K and 1.18 at 693 K which is similar to the trend of Mg self-diffusion [2-4]. However, for diffusion induced processes such as phase transformation and other microstructural changes in the solid state of real polycrystalline Mg-Al alloys, the information on grain boundary (GB) diffusion of Al is also important. Grain boundaries are the most common short circuiting paths for diffusion. GB diffusion can be orders of magnitude faster than bulk volume diffusion, and therefore GB diffusion can play a key role, especially below 0.6 T_m (T_m = melting temperature), in many processes such as precipitation, dissolution, grain growth, coarsening, recrystallization, sintering, etc [5]. Experimental investigations indicate that GB diffusion is dependent on the misorientation between grains [6]. Thus, the study of GB diffusion can provide information on atomic structure and properties of the grain boundary and vice versa.

GB diffusions of ⁶⁵Zn, ⁶⁷Ga and ⁶⁸Ge in Mg have been recently measured by Stloukal and Cermak [7-9] using the radiotracer serial sectioning and residual activity measurement. The misorientation of grain boundary was not determined in their experiments. According to the experimental data, the GB diffusion coefficient of Zn is 3.22×10^{-13} m²/s at 598 K which is about three orders of magnitude higher than the volume diffusion coefficient determined by the present authors using a Mg single crystal diffusion couple [10]. However, no data for GB diffusion of Al in Mg is available.

The present study is focused on the investigation of GB diffusion of Al in polycrystalline Mg using a polycrystalline Mg crystal diffusion couple with Al between 603 and 693 K. In order to accurately determine the Al concentration profiles through grain boundaries with a wide range of grain misorientation, a Hitachi SU-8000 cold field-emission scanning electron microscope (CFE-SEM) equipped with an XMax silicon drift detector (Oxford Instruments) energy dispersive spectrometer (EDS) at McGill University was used.

7.3. Experimental

7.3.1. Sample preparation

Diffusion couple experiments were performed between polycrystalline Mg (99.99 wt. %, Magnesium Elektron) and Al (99.99 wt. %, Alfa Aesar). Small half-circular (15 mm diameter and 10 mm thick) specimens of Mg and Al were annealed at 773 K under a high purity Ar (5N) atmosphere for one week to relieve any stresses induced during the sample preparation. The sizes of Mg and Al grains after the annealing were typically larger than 1000 μ m. The final polishing before coupling was carefully performed with 0.25 μ m oil base diamond suspension (Buehler) to avoid surface oxidation. The polished samples were then tightened with a steel clamp to make sure diffusing surfaces were in perfect contact. The diffusion couple annealing experiments were performed in a tube furnace at 603, 638, 673 and 693 K for 72 hours. To minimize the oxidation at the diffusion interface, the diffusion couple samples were wrapped with Ta foil and an Ar (5N) gas flow was maintained at a rate of 10 ml/min during the annealing experiments. After the annealing experiment, the diffusion couple specimens were quenched in ice cold water, cut perpendicular to the diffusion contact plane with a low speed diamond saw (Buehler IsoMet), grounded and fine-polished with 0.05 μ m OPS (Buehler) solution. A detail experimental procedure can be found in the previous works [1, 10].

7.3.2. Characterization and microanalysis

Quantitative microanalyses of Al in hcp Mg grain and GB were carried out using a Hitachi SU-8000 CFE-SEM equipped with an XMax silicon drift detector EDS. An accelerating voltage of 5 kV with a 1.5 nA beam current was used for line scanning and imaging of the GB. A dwell time of 5 seconds at each point was used with a step size 0.3 µm. The probe size was between 5 and 10 nm. Electron backscattered diffraction (EBSD) analysis was performed with an accelerating voltage of 20 kV, a probe current of 5 nA and a step size of 5 µm using a Nordlys II camera controlled with the HKL Channel 5 system (Oxford Instruments). The quantitative Al concentration in hcp Mg solid solution region (grain) was then extracted using the f-ratio method developed by Horny et al. [11]. This method is similar in approach to the Cliff-Lorimer [12] method used in analytical transmission electron microscopy. The ratio of the intensity of a specific characteristic x-ray normalized by the sum of the x-rays from all elements of the materials is calculated and compared with that calculated with x-ray intensities obtained by Monte Carlo simulations. The theoretical calibration curve was obtained by Monte Carlo modeling using the MC X-ray software [13]. This technique is particularly suited to quantitative x-ray microanalysis in cold FE-SEM as the ratio of x-ray intensities anneals the probe current term and full advantage can be taken from the high brightness and spatial resolution of those instruments. The f-ratio method was used previously on Al-Mg diffusion couples and provided precise quantitative measurements at low accelerating voltage with high spatial resolution [1, 14]. An electron probe micro-analyzer (EPMA) combined with wavelength dispersive spectrometers (WDS) was used to determine the bulk diffusion of Al in hcp Mg for the comparison with results from CFE-SEM EDS. An accelerating voltage of 5 kV was used with a 30 nA beam current, a probe size of about 500 nm, and counting times of 20 seconds on peaks and 20 seconds on background (detection limit was 0.05 wt. %). Points for the line scans through the interface were acquired every 1 µm. Quantitative EPMA results were obtained by correcting the raw data with the PRZ model using pure Al and Mg as standards. The CFE-SEM-EDS and EPMA-WDS results were in strong agreement.

7.4. Results and discussion

Typical secondary electron (SE) image and EBSD map at the diffusion interface are presented in Fig. 7.1. The interface of the diffusion couple sample shows the formation of Mg₁₇Al₁₂ and Mg₂Al₃ intermetallic layers. The diffusion couple cross-section was characterized at the interface by EBSD mapping. This permitted the identification of the GB position and to measure the misorientation angles between the analyzed grains. EBSD was performed with a tilt angle of 70 $^{\circ}$ in relation to the specimen surface normal, and x-ray microanalysis spectra were recorded at 0 ° tilt. To identify precisely the GB position at 0 ° tilt, electron channeling pattern imaging (ECCI) was used [15], where the backscattered electron (BSE) contrast is dependent on the crystal orientation in relation to the beam direction. The estimated spatial resolution of ECCI with an accelerating voltage of 5 kV is of the order of 10 nm in Mg. ECCI has the capability of identifying the exact GB position prior to the EDS line scanning (Fig. 7.2). The EBSD map at the polycrystalline hcp Mg solid solution interface shows that the intermetallics of Mg₁₇Al₁₂ and Mg₂Al₃ are not single crystal; each intermetallic layer is formed of polycrystalline intermetallic grains. The exact misorientation angle between the hcp Mg grains was extracted from the EBSD map prior to quantitative line scanning through the GB and only high angle GBs were selected for microanalysis. Points were selected very carefully along the GB to extract the Al concentration profile. Horizontal arrows on the EBSD map in Fig. 7.1 show the misorientation angles between the grains, whereas the inclined lines show the line scanning directions along the GBs. In order to compare with the Al profiles of GB, an intra-grain (G1 and G2 in Fig. 7.1) Al profile was also determined in the middle of large grain (500 µm apart from the GBs; to make sure no noticeable influence by GB diffusion). Clearly, the GB diffusion of Al is much faster than bulk volume diffusion. It should also be noted that the Al concentration profiles along the GBs are noticeably different depending on the misorientation between two adjacent Mg grains. The higher misorientation between Mg grains, the faster GB diffusion of Al.

When solute diffuses through a GB, a certain amount of solute from the GB can also diffuse into adjacent grains. Depending on the temperature, grain size and difference between GB diffusion

and volume diffusion, three types of concentration profiles induced by GB diffusion can be observed in the materials as described by Harrison [16]: Diffusion through the entire material (Aregime), mainly through GB (B-regime) and only through GB (C-regime). In order to identify the regime of the present GB diffusion, the concentrations of Al perpendicular to the diffusion direction (that is, parallel to diffusion interface) were measured. Fig. 7.2 shows a backscattered electron (BSE) image ECCI of GB1 region in Fig. 7.1 and the concentration profiles of Al analyzed from GB1 toward the Mg grain at different distances (5, 15 and 30 µm) from the intermetallic Mg₁₇Al₁₂ layer. In the Al concentration profiles, Al contents at the middle of grain, 500 µm apart from GB, were also marked as references of volume diffusion of Al: 0.287, 0.009, and 0.0 at.% Al at 5, 15 and 30 µm, respectively. The Al profile at 5 µm shows the highly concentrated Al (5 at. %) at the GB which can induce Al diffusion to adjacent grain up to about 50 µm at 603 K. The infected diffusion area from GB diffusion can be reduced drastically with distance from the diffusion couple interface, and the Al volume diffusion distance becomes only about 15 µm at 30 µm from the interface. As can be seen in Fig. 7.1, the GB diffusion length of GB1 is more than 70 µm. Thus, the current GB diffusion is corresponding to the B-regime according to the definition by Harrison [16]. Of course, the infected bulk zone by GB diffusion becomes larger with increasing temperature. For instance, Al content at GB, 15 µm apart from the interface for the sample annealed at 673 K, is 8.375 at. % Al and can induce the volume diffusion to adjacent grain up to about 250 µm.

Concentration profiles of Al through grain boundaries were reproduced with a multiphase diffusion model [1, 10] to determine GB diffusion coefficients of Al in hcp Mg. In the simulation, the interdiffusion coefficients of two intermetallic phases were taken from the experimental values [1], diffusion of Mg in GB is unknown. So the Mg self-diffusion coefficient [3] was multiplied by the same factor as Al diffusion coefficient to reproduce the Al profile at GB. During simulation, it is assumed that the loss of Al toward grains adjacent to the GB has no significant (B-Regime [16]) influence to the GB diffusion. The diffusion coefficient of Al for each specific GB is plotted in Fig. 7.3 along with the bulk diffusion coefficient of Al in Mg determined from Mg single crystal diffusion couple experiments [1] using the same simulation method. The calculated concentration profiles of Al from the GB diffusion coefficients of Al

dependent on misorientation are plotted in Fig. 7.1 as solid lines, which are well matched with experimental data.

The calculated GB diffusion coefficients of Al are highly dependent on the misorientation angle of the GB. In general, the GB diffusion coefficient of Al becomes higher with increasing misorientation angle. The GB diffusion coefficient of Al with misorientation of about 75 ° is around two orders of magnitude larger than volume diffusion coefficient. Trunbull [6] performed GB diffusion studies in silver between 673 and 798 K using from 9 to 28 ° misorientation GB in a bicrystal and found that the self-diffusion coefficient of Ag along GB increases with increasing misorientation, and is more prominent at high angle misorientations like 28 °. The difference between GB and volume diffusion of Al in Mg becomes larger at lower temperature as expected. That is, the activation energy of GB diffusion (slope of the GB diffusion line in Fig. 7.3) is lower than that of volume diffusion. At 693 K, as can be seen in Fig. 7.3, the calculated GB diffusion coefficients deviate from results obtained at lower temperatures. Due to the loss of a large amount of Al in bulk through volume diffusion to adjacent grains, the apparent GB diffusion coefficient calculated based on the Al profile at the GB in the sample at 693 K becomes lower than the trend derived from the results at lower temperatures. Therefore, the experimental data at 693 K were not taken into account in the evaluation of the GB diffusion coefficient of Al. of course, even at low temperature; there is still a certain loss of Al in bulk due to volume diffusion to adjacent Mg grains. Therefore, the real GB diffusion coefficients should be slightly higher than our measurement in Fig. 7.3.

7.5. Summary

In summary, for the first time the GB diffusion coefficient of Al for polycrystalline Mg was determined quantitatively using diffusion couple experiments with high resolution CFE-SEM EDS analysis. It is found that the GB diffusion coefficient of Al is highly dependent on the misorientation of adjacent grains. The GB diffusions coefficient of Al at a misorientation of

about 75 ° is around two orders of magnitude higher than that of volume diffusion coefficient of Al in hcp Mg at the temperatures between 600 and 700 K. The difference between GB diffusion and volume diffusion can become larger at lower temperatures. This indicates that GB diffusion can play an important role in many diffusion driven processes such as diffusion induced grain migration, dissolution, coarsening, precipitation, and grain growth for Mg alloys at low temperatures (in particular below about 600 K). This study also shows that diffusion couple experiments with high resolution CFE-SEM can be used to investigate GB diffusion of solute in Mg alloys.

7.6. Acknowledgements

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Fig. 7.1. Diffusion couple interface at 603 K after 72 hours: (top) SE image and EBSD map with misorientation angles and line scanning direction, (bottom) Al concentration profiles along GB and through bulk with diffusion modeling results.



Fig. 7.2. Diffusion couple interface at 603 K after 72 hours: (left) BSE image (ECCI) with line scanning direction at various positions across GB, (right) Al concentration profile across GB in comparison with bulk Al concentration.



Fig. 7.3. Al diffusion coefficients in GB with various misorientation angles in comparison with bulk diffusion [1]. *in grain: the volume diffusion coefficient of Al determined at 603 K from the present study.

Chapter – 8

Effect of the Basal Plane Orientation on Al and Zn Diffusion in hcp Mg

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision.

8.1 Abstract

Diffusion couple experiments for Mg-Al and Mg-Zn systems with polycrystalline Mg were performed between 638 and 693 K (365 and 420 °C) and 553 and 593 K (280 and 320 °C), respectively, to determine the diffusion of Al and Zn in Mg crystal depending on the orientation of basal plane of hcp Mg. Solute (Al and Zn) diffusion coefficient decreases linearly in Mg crystal from the basal plane towards normal to the basal plane.

Keywords: diffusion, magnesium alloy, aluminium, zinc, diffusion couple experiment.

8.2. Introduction

Magnesium is the lightest commercially viable structural metallic material. However, industrial usage of Mg alloy is still far below its expected potential due to its low room temperature formability. Mg hexagonal close packed (hcp) structure produces highly inhomogeneous deformations due to its inherent limitation of active slip systems. Therefore, the texture of hcp Mg can have a significant influence to the thermo-physical and mechanical properties of Mg alloy. Diffusion kinetics is an important physical property which can influence many material processing phenomena such as phase transformation, homogenization, precipitation, recrystallization, creep, etc.

The anisotropic diffusion behaviors of Al and Zn in hcp Mg were recently studied by the present authors [1, 2] using Mg single crystal diffusion couple technique. According to the experimental results, the diffusions of both Al and Zn through the basal plane of Mg are slightly faster than that perpendicular to the basal plane: $D\perp/D\parallel$ of Al in hcp Mg = 1.33 at 638 K (365 °C) and 1.18 at 693 K (420 °C), and $D\perp/D\parallel$ of Zn in hcp Mg = 1.23 at 553 K (280 °C) and 1.17 at 603 K (320 °C). In this study, we investigate the variation of diffusion coefficients of Al and Zn in hcp Mg depending on the orientation of hcp Mg crystal from 0 to 90° rotation from the c-axis.

8.3. Experimental methodology

To determine the Al and Zn diffusions in different orientation of hcp Mg crystal, polycrystalline Mg diffusion couples with Al and Zn were used. The orientations of Mg grains at the diffusion interface were determined by X-ray Diffraction (XRD) and the concentrations of Al and Zn in differently orientated Mg grains were analyzed by Electron Probe Micro Analyzer with a Wavelength Dispersive Spectroscopy (EPMA-WDS). Then, the diffusion coefficients of Al and Zn and Zn were calculated using the multiphase diffusion model [1, 2] and a Gaussian solution for the Fick's diffusion equation [3]. The details are explained below.

Polycrystalline Mg (99.99 wt. %, Magnesium Elektron), Al and Zn (99.99 wt. %, Alfa Aesar) specimens were annealed at 773 K (500 °C) under high purity Ar (5N) atmosphere for one week to obtain a starting materials with large grain size and relieve any stress during preparation. The grain size of polycrystalline Mg was typically larger than 1000 µm after annealing. Al and Zn were coupled with Mg and annealed again in Ar (5N) atmosphere in a tube furnace according to standard procedure [1, 2]. Diffusion couples were tied by steel clamp and wrapped with Ta foil to minimize oxidation. Diffusion annealing experiments of Mg-Al couples were performed between 638 and 693 K (365 and 420 °C) for a maximum 3 days to obtain well diffused specimens. Diffusion annealings of Mg-Zn couples were carried out between 553 and 593 K (280 and 320 °C) for a maximum 4 days due to the low eutectic temperature of the Mg-Zn system. After diffusion annealing, specimens were cold mounted and cut perpendicular to the diffusion contact plane with a low speed diamond saw (Buehler IsoMet). Polishing was then performed with 3 and 1 µm diamond slurry and 0.05 µm colloidal silica (OPS, Buehler) and etching was executed with acetal-picral solution (4.2 g picric acid, 10ml H₂O, 10ml acetic acid and 70 ml ethanol) by carefully immersing the samples in the etchant for 4 to 5 seconds and then cleaning their surface with running water and ethanol. Samples were then observed with an optical microscope (Nikon-Clemex vision).

8.4. Results and Discussion

An optical image of the Mg-Al diffusion couple annealed at 693 K for 3 days is shown in Fig. 8.1. At the diffusion interface, intermetallic layers of $Mg_{17}Al_{12}$ and Mg_2Al_3 are formed in Mg/Al diffusion couples. A clear indication of the success of the diffusion couple experiments is to check the growth constant of intermetallics. The present experimental growth rates of intermetallics (for example, 7.89×10^{-14} and 4.08×10^{-13} for $Mg_{17}Al_{12}$ and Mg_2Al_3 at 693 K, respectively) are consistent with the well-established data by the authors for Mg/Al [1] and Mg/Zn [2] diffusion couples. As can be seen in Fig. 8.1, there are many large Mg grains at the diffusion interface. The grain size of Mg was not significantly different from the pre-annealed starting polycrystalline Mg. Typical Scanning Electron Microscope Backscattered Electron

(SEM BSE) images of the intermetallic layers of Mg/Al and Mg/Zn diffusion couples can be found in our previous studies [1, 2]

The orientations of Mg grains at the diffusion interface were determined with XRD using a Bruker Discover D8 diffractometer equipped with HiSTAR area detector and a Co target. Maps of the $\{0001\}$, $\{10\overline{1}0\}$ and $\{10\overline{1}1\}$ orientations were measured between 5.1 and 6.2 ° polar and radial steps up to a maximum tilt of 81.6 ° at the center of each selected large grain. The x-ray source was fixed at the center of each grain for point analysis without any oscillation. Orientation distribution functions (ODF) were calculated from these maps, also known as pole figures, according to the procedure described by Bunge [4] with the aid of the software Tex Tool 3.3. Recalculated pole figures were then derived from the ODFs. Results of the orientations of Mg grains at the diffusion interface are presented in Fig. 8.2. Note that the x-ray signals were only detected from one single grain of Mg in each case due to the large grain size of Mg which allowed successful measurement of the ODF of each Mg grain.

For each diffusion couple sample, the orientation of many Mg grains adjacent to the diffusion interface (intermetallic phase) were analyzed using the XRD pole figure measurement described above. Then, four grains, which had orientation (tilting angles from c-axis of hcp Mg crystal) widely spread between 0 to 90°, were selected for composition analysis of Al and Zn. Each diffusion bonded specimen was slightly polished with 0.05 μ m OPS to remove the etchant effect. Quantitative microanalyses of Al and Zn in the bulk hcp Mg for those specific large Mg grains were carried out to find Al and Zn concentration profiles using a JEOL 8900 EPMA-WDS. An accelerating voltage of 15 kV was used with a 20 nA beam current, a spot size about 1 μ m, and counting times of 20 seconds on peaks and 20 seconds on background. Microanalyses were performed using line scanning with a step size of 2 μ m. Raw data were reduced with the PRZ corrections using pure Mg, Al and Zn. The detection limit of WDS was 0.05 wt. %. Reproducibility of Al and Zn concentration profiles was confirmed by acquiring several line scans within each grain. In order to avoid any grain boundary diffusion effect, the composition analyses were done from intermetallic layer to the center of Mg grain.

Typical examples of concentration profiles of Al and Zn in Mg/Al and Mg/Zn diffusion couples after diffusion annealing are depicted in Fig. 8.3. WDS concentration profiles of Al in hcp Mg crystal annealed for 3 days at 673 K (400 °C) were collected for basal plane tilted at 10, 25, 55, and 70 °, respectively (Fig. 8.3 (a)). The diffusion depth of Al in hcp Mg grain decreases with increasing tilting angle towards normal to basal plane, which means that the diffusion of Al becomes slower with increasing tilting angle from basal plane. Zn concentration profiles at 573 K (300 °C) after 4 days of annealing are also shown for basal plane tilted at 40, 50, 55, and 70 °, respectively (Fig. 8.3 (b)), which shows the same trend as Al.

To calculate the diffusion coefficients of Al and Zn in hcp Mg crystal in preferred orientation, a multiphase diffusion simulation [1, 2] was performed. In the simulation, pre-known diffusion values, like Mg self-diffusion coefficients and interdiffusion coefficients of intermetallic phases were used. By reproducing the experimental diffusion profiles of Al and Zn in hcp Mg, the diffusion coefficients of Al and Zn were then determined. In the simulation, the chemical potentials (thermodynamic driving forces) of Mg and solutes (Al and Zn) can be obtained from the FTlite thermodynamic database [5]. The other common method used to determine the diffusion coefficients of solute (strictly speaking, the impurity diffusion coefficients) is given by Jost [3]. It is a Gaussian solution of the Fick's diffusion equation for a constant diffusivity and a specific geometry of the specimen under the very dilute region. The applications of these two methods to diffusion couple experiments are already demonstrated in our previous study [2]. In the present these two techniques were used to determine the impurity diffusion coefficient of Al and Zn and Zn in hcp Mg crystal.

Impurity diffusion coefficients of Al and Zn depending on the orientation of hcp Mg crystal are shown in Fig. 8.4. In the figure, the Mg single crystal data [1, 2] at the 0 and 90 ° orientations are also shown for comparison. The present experimental data show that the diffusions of Al and Zn in hcp Mg are linearly decreasing with increasing tilting angle toward normal to basal plane.

8.5. Summary

The difference in the diffusion of solute in hcp Mg depending on the orientation of hcp Mg is not so significant (the maximum difference is still less than 1.4 times in the experimental temperature ranges). There is no anomaly in the diffusion of Al and Zn in hcp Mg depending on the orientation of Mg. The dependence of diffusion coefficients of Al and Zn on the orientation of hcp Mg becomes less significant at higher temperature. From the present results of Al and Zn and also previous results of other solutes like Cd, In, Sb Sn, etc. [6], we can conclude that the diffusion coefficient of each solute element in hcp Mg is less significantly dependent on the orientation of hcp Mg crystal but the diffusion coefficients of solute can be more largely varied depending on solute element itself.

8.6. Acknowledgements

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8.7. References

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Fig. 8.1. Optical micrograph of polycrystalline Mg and Al diffusion couple after diffusion annealing at 693 K (420 °C) for 3 days.



Fig. 8.2. XRD pole figures of basal plane in hcp Mg crystals at the diffusion interface of Mg/Al diffusion couples with schematic tilted crystal orientation.



Fig. 8.3. Solute concentration depending on the tilting angle of hcp Mg crystal from its basal plane: (a) Al concentration profile for Mg-Al diffusion couple after 3 days annealing at 673 K (400 °C), and (b) Zn concentration profile for Mg-Zn diffusion couple after 4 days annealing at 573 K (300 °C).



(b)

Fig. 8.4. Impurity diffusion coefficients of Al and Zn in hcp Mg depending on the Mg crystal orientation. 0 and 90 °. Filled symbols are from the previous Mg single crystal diffusion experiments [1, 2].

Chapter – 9

Experimental and diffusion simulation for the homogenization of as cast Mg-Al, Mg-Zn and Mg-Al-Zn alloys

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As a first author of this article I performed all the experiments, analysis, calculations and wrote the manuscript. Dr. D. H. Kang assisted as a post-doctoral fellow in the homogenization experiments and sample preparations. Prof. I. H. Jung who is the principle investigator contributed to critical analysis and supervision. All the co-Authors provided valuable suggestions and comments and reviewed the manuscript before submission.

9.1 Abstract

Annealing of as cast Mg-Al alloys (3, 6 and 9 wt. % Al) and Mg-Zn alloys (1.5, 4.0 and 5.5 wt. % Zn) were performed at 603 and 673 K (330 and 400 °C) for 1, 2, 4, and 8 hrs to systematically investigate the variation of second phase fraction and solute concentration profile in Mg matrix using SEM image analysis and EMPA-WDS, respectively. To calculate second phase fraction and solute concentration profile, a diffusion model considering the moving boundary was constructed, and the experimental results were successfully explained by the model. The expansion of model to ternary Mg-Al -Zn alloy is also described. This model can be used for the optimization of homogenization process of the Mg alloys.

Keywords: magnesium alloys, aluminium, zinc, annealing, homogenization, dissolution.

9.2. Introduction

Magnesium and magnesium based alloys are receiving global attention, due to its superior light weight characteristics, especially in transport sector. The most common commercial Mg alloys are AZ (Al and Zn), ZA (Zn and Al), AM (Al and Mn) and AS (Al and Si) series which are used both as cast and wrought products. Although the cast Mg products have been widely used in automotive and electronic applications, the commercialization of wrought Mg alloys are still slower than its potential because of their limited room temperature formability, low creep resistance and inferior high temperature mechanical properties. Therefore, active research is being carried out to understand the deformation process and improve the formability of Mg alloys.

The first process of wrought Mg production is typically the homogenization (solution treatment) of cast Mg product. The purpose of this process is to dissolve the second phase and homogenize as cast microstructure as much as possible to provide optimum microstructure for subsequent rolling or extrusion process. The temperature and time for homogenization of Mg alloy are dependent on the as cast microstructure which is varied with casting condition and alloy composition. Typical homogenization process for AZ alloys in industry is carried out at higher than 603 K (330 °C) for more than several hours [1-3]. The homogenization process is time consuming and requires high temperature, and hence optimization of the process is essential for cost competition. However, there is no systematic study on the homogenization of binary Mg-Al and Mg-Zn and ternary Mg-Al-Zn alloys available in open literature.

Recently, the present research group performed systematic casting experiments for Mg-Al, Mg-Zn and Mg-Al-Zn alloys using various casting techniques [4-6]. The main purpose of the casting experiments was to understand the evolution of as cast microstructure depending on casting condition and alloy composition and to develop the solidification model to predict the as cast microstructure. Simultaneously, the present authors have also investigated the diffusion kinetics
of Mg-Al and Mg-Zn alloys using diffusion couple experiments [7-8] to find out the diffusion coefficients in the binary alloys. These diffusion coefficients of Al and Zn in hcp Mg and interdiffusion coefficients of Mg-Al and Mg-Zn intermetallic phases are essential to understand the homogenization of microsegregation and dissolution of second phase in solution treatment.

The purpose of the present study is the systematic experimental investigation on the microstructural change of various Mg-Al (3, 6 and 9 wt. % Al) and Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) alloys during homogenization process. In addition, a homogenization model based on the diffusion simulation is developed for binary Mg-Al and Mg-Zn and ternary Mg-Al-Zn alloys. Eventually, this homogenization model will be combined with our solidification model to predict the microstructural evolution of Mg alloys for casting and homogenization processes.

9.3. Experimental

Cast samples of Mg-Al alloys (3, 6 and 9 wt. % Al) and Mg-Zn alloys (1.5, 4.0 and 5.5 wt. % Zn) were prepared using rectangular plate shape and wedge shape water cooled Cu molds. The chemical compositions of alloys were confirmed by spark spectrometer (Optical Emission Spectroscopy) and ICP (Inductive Coupled Plasma) analysis. The cooling rate of 80 K/sec was obtained in the plate casting and various cooling rates from over 110 K/sec to 15 K/sec depending on the location were obtained in the wedge casting. The temperature profiles were recorded from the K-type thermocouples inserted in molds and heat transfer simulation. The geometry of cast samples is shown in Fig. 9.1.

For the present homogenization experiment, Mg-Al alloys from plate casting (80 K/sec cooling rate) and Mg-Zn alloys from wedge casting (section where the cooling rate is about 80K/sec) were used. The large plates with 1 cm thickness (see Fig. 9.1) were cut out from the cast products. As cast microstructures of sectioned plates were analyzed under optical microscope to confirm the homogeneity in microstructure. Then, small rectangular specimens $(3.5 \times 1.4 \times 1 \text{ cm})$

were sectioned from large plate samples and the sharp edges of specimens were removed by grinding prior to the homogenization experiments. Parts near the surface of cast product were discarded to avoid heterogeneous chilled microstructure.

The homogenization experiments were carried out at 603 and 673 K (330 and 400 °C) using a box furnace (Carbolite 1500 RTF; inner dimension of 12 cm x 12 cm x 28 cm) with temperature sensitivity of \pm 5 K. The temperatures selected in the present study are the most common temperatures used in the industry for AZ alloys. The furnace was conditioned at annealing temperature for 24 hours prior to annealing experiments. Specimens were placed exactly below the tip of thermocouple in the furnace for the annealing process. The durations of annealing experiments were varied from 1 hr and 8 hrs (1, 2, 4 and 8 hrs). After annealing experiments, specimens were quickly taken out from the furnace and quenched in ice cold water. The color of surface of specimens were cut at the center using a low speed diamond saw (Buehler IsoMet). Polishing of specimen was done first with SiC sand papers (120, 400, 600 and 1200 grit size) to obtain a flat surface and then final polishing were carried out with 3 µm and 1 µm size diamond suspension followed by 0.05 µm OPS (colloidal silica particles, Buehler) solution. To remove residue that might adhere on the specimen surface, ultrasonic cleaning of specimens was done in ethanol for 20 minutes and then dried with hot air.

Philips XL-30 FE-SEM (Field Emission Scanning Electron Microscope) equipped with EDS (Electron Dispersive Spectroscopy) was used to acquire backscattered electron (BSE) images and to identify the second phase ($Mg_{17}Al_{12}$ and $Mg_{51}Zn_{20}$) present in binary Mg-Al and Mg-Zn alloys. Second phase fractions of as cast and annealed specimens were determined from the BSE images. To reduce the statistical error, an area of 3 mm x 3 mm was scanned for each specimen to determine the areas of second phase and matrix with the help of an image analysis technique with Image^J software. The two dimensional area fraction of second phase was considered as same as the phase fraction of second phase in each alloy.

The microsegregation of solute (chemical inhomogeneity of solute like Al and Zn) in Mg grain was investigated mainly using a JEOL 8900 Electron Probe Micro Analyzer (EPMA) Wavelength Dispersive Spectroscopy (WDS). Second phases like Mg17Al12 and Mg51Zn20 usually appear at grain boundaries. Thus, special care is needed in the analysis of the microsegregation in Mg grain. A schematic illustration of EPMA line scan technique for binary Mg-Al and Mg-Zn alloys used in the present study is shown in Fig. 9.2 to obtain microsegregation information in Mg grains. To obtain solute concentration profile in Mg grains across their grain boundaries, at least five EPMA line scans between the centers of two adjacent grains were performed for each specimen. It should be noted that the line scans were done without passing through second phase. In some cases, the composition at the center of grain was obviously higher than other analyses because the center of the grain in the polished section could be off from the core of the grain and those line scans were neglected from the analyses. An accelerating voltage of 15 kV with a 20 nA beam current, a spot size of about 1 µm, and counting times of 20 seconds on peaks and 20 seconds on background was used for the WDS analysis. The line scan was performed using a step size of 2 μ m. Raw data were reduced with the PRZ corrections using pure Mg, Al and Zn standard. The detection limit of EPMA-WDS was 0.05 wt. %.

9.4. Experimental Results

The Mg-rich sides of binary phase diagrams for Mg-Al and Mg-Zn systems calculated from the FactSage FTlite database [9] are presented in Fig. 9.3. According to the calculated phase diagrams, all binary Mg-Al and Mg-Zn alloys can be completely solutionized at 603 and 673 K (330 and 400 °C) except the Mg-Al alloy with 9 wt. % Al at 603 K (330 °C).

The SEM microstructures of as cast and annealed binary Mg-Al (3, 6 and 9 wt. % Al) alloys are shown in Fig. 9.4. As cast microstructures of the Mg-Al alloys show the equiaxed dendrite structure. SEM-BSE images clearly show the microsegregation and second phase in grain boundary. The second phase particles for all binary Mg-Al alloys were determined, from EDS and WDS analyses, to be $Mg_{17}Al_{12}$, as expected. The variation of secondary phase ($Mg_{17}Al_{12}$) amount is plotted in Fig. 9.5. The amount of Mg₁₇Al₁₂ phase in the as cast Mg -3, -6 and -9 wt. % Al samples were 0.85, 2.82, and 3.49 %, respectively. During the annealing of the Mg-Al samples at 673 K (400 °C), the amount of second phase reduced drastically with time. For example, the amounts of Mg₁₇Al₁₂ phase in Mg -3 and -6 wt. % Al samples were reduced below 0.5 % after 2 hrs annealing at 673 K (400 °C) and that of Mg-9 wt. % Al sample became even less than 0.3 % after 8 hrs. The homogenization of the Mg-Al alloys at 603 K (330 °C) was much slower compared to that at 673 K (400 °C). The amount of Mg₁₇Al₁₂ phases in Mg -3 and -6 wt. % Al samples decreased slowly with time. On the other hand, the change in Mg₁₇Al₁₂ amount for Mg-9 wt. % Al sample increased from 3.49 % to 5.50 % after 1 hr, decreased to 2.86 % in 2 hr, then increased again after 2 hrs and finally reached 6.80 % in 8 hrs by the formation of new Mg₁₇Al₁₂ particles mainly in grain boundary. This abnormal behavior can be partially understood from the phase diagram of the Mg-Al system in Fig. 9.3. According to the phase diagram, the equilibrium amount of $Mg_{17}Al_{12}$ is 5.35 wt. % at 603 K (330 °C).

The microstructure of the Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) alloys are shown in Fig. 9.6. Compared with the Mg-Al alloys, the apparent grain size and the size of second phase in the Mg-Zn alloys were much bigger. According to the EPMA WDS analysis for 10 random second particles, the second phase was identified as $Mg_{51}Zn_{20}$. The variation of the second phase $Mg_{51}Zn_{20}$ in the Mg-Zn alloys with annealing time at 603 and 673 K (330 and 400 °C) are presented in Fig. 9.7. The amount of $Mg_{51}Zn_{20}$ in the as cast samples was 0.93, 2.49, and 3.16 % for Mg alloy with 1.5, 4.0, and 5.5 wt. % Zn, respectively. In general, the dissolution rate of second phase in the Mg-Zn binary alloys was faster compared to that in the Mg-Al alloys. For all Mg-Zn alloys, nearly all second phase ($Mg_{51}Zn_{20}$) particles were dissolved completely after 4 hrs annealing at 673 K (400 °C). Although the dissolution rate of $Mg_{51}Zn_{20}$ at 603 K (330 °C) was much slower than that at 673 K (400 °C), the remaining amount of $Mg_{51}Zn_{20}$ were less than 0.3 % after the annealing of 8 hrs at 603 K (330 °C).

The evolutions of Al and Zn solute profiles (microsegregations of Al and Zn) in hcp Mg grain with annealing time are plotted in Figs. 9.8 and 9.9. As illustrated in Fig. 9.2, the line scan analyses were carried out between the cores of two adjacent grains without crossing second phase particles at the grain boundary. As cast composition profiles clearly shows a drastic change in solute composition with distance from core to grain boundary. According to the experimental results, neither Mg-Al nor Mg-Zn alloys could be completely homogenized even after 8 hrs annealing at 603 K (330 °C). Of course, the inhomogeneity in Al and Zn concentrations became more severe at high Al and Zn containing alloys. On the other hand, all as cast Mg-Al alloys were almost fully homogenized after 8 hrs annealing at 673 K (400 °C), and as cast Mg-Zn alloys were homogenized after 4 hrs of annealing at the same temperature. These results are consistent with the second phase fraction analyses in Figs. 9.5 and 9.7.

In the case of the Mg-3 wt. % Al and Mg-1.5 wt. % Zn alloys, the average solute content from the line scans of the as cast alloys in Figs. 9.8 and 9.9 was already similar to the original nominal composition of each alloy. The amount of second phase in these two alloys was about 1 % or less in the as cast state (see Figs. 9.5 and 9.7), which means that most of Al and Zn were in hcp solid solution. Therefore, the incremental of solute content in matrix by the dissolution of small amount of second phase during homogenization process was insignificant. On the other hand, the average solute contents from the line scans for the other alloys were significantly increasing with homogenization time by the dissolution of second phases, and finally reached the normal solute concentration of the alloys after full homogenization.

9.5. Diffusion calculations for homogenization process

9.5.1. General diffusion model

To explain the dissolution of second phase particles and evaluation of compositional inhomogeneity in Mg grain during the homogenization, two dimensional or three dimensional Page | 195

phase field simulation can be performed considering the exact as cast microstructural feature. However, such simulation is computationally very time consuming and complex. Therefore, a simple one dimensional (1D) diffusion simulation model is proposed in this study to explain the homogenization process. This 1D model contained two phases (hcp Mg phase and second phase) to simulate the dissolution of second phase, which is treated as moving boundary between hcp and second phase. The interface compositions assumed to be constant equilibrium throughout the diffusion process with various time at given temperatures. The moving boundary problem was solved by the flux balance equation adopting "Murray-Landis" transformation approach [10]. The diffusion equation was solved using a finite difference method (FDM). The more details of the calculation procedure are explained below.

The diffusions in hcp Mg phase and second phase (intermetallic phase) in the binary system can be solved using the Fick's second law:

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x} \left(D_k \frac{\partial C_k}{\partial x} \right) \tag{9.1}$$

where C_k is the concentration of solute k, t the time, x the distance, and D_k the diffusion coefficient of solute k. In the case of hcp Mg phase, the diffusion coefficient (D_k^{hcp-Mg}) of solute k can be composition-dependent, which can be expressed by the following equations in combination with thermodynamic chemical potential [11]:

$$D_k^{hcp-Mg} = D_{kk}^{hcp-Mg} - D_{Mgk}^{hcp-Mg}$$

$$\tag{9.2}$$

$$D_{kk}^{hcp-Mg} = y_k y_{Mg} \Omega_k^{hcp-Mg} \frac{d\mu_k^{hcp-Mg}}{dy_k}$$
(9.3)

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$$D_{Mgk}^{hcp-Mg} = y_k y_{Mg} \Omega_{Mg}^{hcp-Mg} \frac{d\mu_{Mg}^{hcp-Mg}}{dy_k}$$

$$(9.4)$$

where y_i is the mole fraction or site fraction of *i*. Ω_i^{hcp-Mg} is the mobility of *i* and μ_i^{hcp-Mg} is the chemical potential of *i* in hcp Mg solution (with respect to hcp structure). In the case of the second phase (intermetallic phase), the composition-independent interdiffusion coefficient can be used.

In solving the dissolution of second phase in hcp Mg phase, the most critical part is the moving boundary problem (also known as Stefan problem) at the interface between hcp Mg and second phase. Different approaches have been designed by many researchers to solve the moving boundary problem [12-16]. The flexible-grid scheme/variable space grid is one of the most popular approaches in which the total grid expands/shrinks to match the interface motion. The most common method of shifting the grid positions and adjusting the grid concentrations is the so-called "Murray-Landis" transformation [10]. In the present study, the moving boundary problem was also treated by the Murray-Landis transformation using an explicit method. The Murray-Landis transformation has been applied to moving boundary problems occurring in multiphase diffusion couple calculations by the present authors for the Mg-Al [7], Mg-Zn [8] and Mg-RE [17] systems.

The Murray-Landis transformation involves the transformation of the concentration-distance profile to allow for the movement of the phase interfaces. In order to consider moving interface, the diffusion equation can be expressed as:

$$\frac{dC_n^p}{dt} = \frac{\partial C_n^p}{\partial x_n^p} \left(\frac{dx_n^p}{dt} \right) + \frac{\partial C_n^p}{\partial t}$$
(9.5)

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where *n* is total number of grid of left-side phase (in this study, hcp Mg phase), and (dx_n^p/dt) is the velocity of interface (n_{th} grid) of *p* phase (left-side phase; hcp Mg phase). The velocity of p+1 phase (right-side phase; intermetallic phase) at the interface (n_{th} grid) with *p* phase has the same velocity as (dx_n^p/dt) . dx_n^p/dt at the interface for n_{th} grid can be calculated using the flux balance equation [18] with four-point approximation formula for concentration gradient with distance.

$$\left(\frac{dx_n^p}{dt}\right) = \left\{ D^{IMC} \left(\frac{\partial C_n}{\partial x}\right)_{n,IMC} - D^{hcp-Mg} \left(\frac{\partial C_n}{\partial x}\right)_{n,hcp-Mg} \right\} / (C_n^{hcp-Mg} - C_n^{IMC})$$
(9.6)

The compositions of hcp Mg and second phase (IMC) at the interface are assumed to be equilibrium compositions. A complete diffusion equation can be constructed by inserting Eqs. (9.1) and (9.6) into Eq. (9.5), and this equation can be solved numerically using FDM.

In the diffusion calculation, the chemical potentials μ_k^{hcp-Mg} and μ_{Mg}^{hcp-Mg} and equilibrium composition for hcp Mg and second phase at the interface were calculated from the critically evaluated thermodynamic database for Mg alloys (FactSage FTlite database) [9]. Regarding the diffusivity coefficients, the mobility of Mg in hcp Mg (Ω_{Mg}^{hcp-Mg}) was derived from the selfdiffusion coefficients of Mg determined by Combronde et al. [19], the other mobility values Ω_k^{hcp-Mg} and interdiffusion coefficients of Mg₁₇Al₁₂ and Mg₅₁Zn₂₀ phases were taken from previous studies by the present authors [7, 8]. All the diffusivity values used in the present study are summarized in Table 9.1. The molar volumes of hcp phase (14.0304 cm³/g-atom) and second phase (Mg₁₇Al₁₂:12.5884 cm³/g-atom, Mg₅₁Zn₂₀:11.9537 cm³/g-atom) were taken from FactSage FTlite database [9] and were assumed to be constant for the sake of simplicity.

9.5.2. Diffusion calculation results

Numerical simulation results for the dissolution of $Mg_{17}Al_{12}$ phase in hcp Mg of Mg-9 wt. % Al alloy at 673 K (400 °C) are shown in Fig. 9.10. In the simulation, initial total length of hcp and $Mg_{17}Al_{12}$ phase together was assumed to be 25 µm and the length of $Mg_{17}Al_{12}$ was assumed to be 0.875 µm out of 25 µm (this is the same as second phase fraction analyzed from BSE image analysis in Fig. 9.5). The initial Al composition profile of hcp Mg phase used in the simulation was taken from the EPMA scan from the core of grain to grain boundary (see Fig. 9.8) and the composition of $Mg_{17}Al_{12}$ was assumed as its eutectic composition. The interfacial compositions of hcp Mg and $Mg_{17}Al_{12}$ phase were taken from equilibrium calculations of FactSage FTlite database [9]. The initial grid size of hcp Mg phase was 0.25 µm and that of $Mg_{17}Al_{12}$ was 0.1 µm.

The calculated second phase fractions of $Mg_{17}Al_{12}$ and $Mg_{51}Zn_{20}$ phase in the Mg-Al and Mg-Zn alloys with annealing time were plotted in Fig. 9.11 along with experimental data. As mentioned above, the length fraction of second phase in the simulation was considered as volume fraction (area fraction from BSE image) of second phase in the experiments. The calculated results are in excellent agreement with experimental dissolution rate for all alloys at both 603 and 673 K (330 and 400 °C). The dissolution of $Mg_{17}Al_{12}$ phase in Mg-9 wt. % Al at 603 K (330 °C) was not calculated because there was the formation of $Mg_{17}Al_{12}$ phase rather than the dissolution of the phase at this temperature as can be seen in Fig. 9.5 (a).

In the simulation of solute profiles in Mg grain across the grain boundary in Figs. 9.8 and 9.9, a simple diffusion simulation considering only hcp Mg solid solution was carried out. That is, the simulation was done using Eq. (9.1) without considering the moving boundary. In the simulations, the experimental as cast compositional profiles were used as the initial solute profiles. As mentioned earlier, the dissolution of second phase particles at grain boundary (although the particles are not located at the line scan region) can increase the overall solute

composition of Mg grain during the homogenization process. Therefore in the present 1D homogenization model, the results of second phase dissolutions in Fig. 9.11 are used for the correction of solute composition during the homogenization of microsegregation. That is, the above simulation of the dissolution of second phase was conducted first to provide the dissolution rate of second phase with time. This result was then converted to the incremental amount of solute in Mg grain with time. This increment of solute was added up to the concentration of each node prior to starting next time step calculation in the simulation for homogenization in Fig. 9.8 and 9.9. The initial grid size of hcp Mg phase was 0.25 μ m and time step was 1 ms. Zero mass transfer was considered during diffusion calculation in both ends for the one dimensional single hcp Mg solid solution. As can be seen in Figs. 9.8 and 9.9, the present homogenization model can reasonably well reproduce the variations of concentration profiles of both Mg-Al and Mg-Zn alloys during the homogenization process.

The homogenization model can be expanded to ternary Mg-Al-Zn system for AZ series alloys. The main change is the expression of diffusion coefficient of solute in hcp-Mg in the ternary system. General expression for diffusion of k (Al and Zn) in hcp Mg can be expressed with above mentioned variable as follows [11]:

$$\frac{\partial C_k}{\partial t} = \sum_j \frac{\partial}{\partial x} \left(D_{kj} \frac{\partial C_j}{\partial x} \right)$$
(9.7)

$$D_{kj} = \sum_{i} \left(\delta_{ik} - y_{k} \right) y_{i} \Omega_{i} \left(\frac{\partial \mu_{i}}{\partial y_{j}} - \frac{\partial \mu_{i}}{\partial y_{Mg}} \right)$$
(9.8)

where *k* and *j* are solutes like Al and Zn, and *i* is Mg, Al, and Zn, *C* is the composition of solute, *D* the diffusion coefficient in hcp-Mg, *x* distance, *y* the site fraction, δ_{ik} kronecker delta, Ω the mobility, μ the chemical potential (relative to hcp state). Two main interdiffusion coefficient and two interactive interdiffusion coefficients can be calculated from Eq. (9.8) for ternary Mg-Al-Zn alloy system.

No homogenization experiment was carried out for ternary Mg-Al-Zn (AZ) alloy, hence, artificial as cast microstructural input was used for the homogenization simulation. To simulate the homogenization of AZ31 alloy, for example, the as cast concentration profiles of Al and Zn of binary Mg-3 wt. % Al and Mg-1.5 wt. % Zn in Fig. 9.8 and 9.9 were taken as initial microsegregation in Mg grain for AZ31 alloy. The grain size was assumed to be 40 μ m (that is, the diffusion was simulated as 40 μ m) similar to binary Mg-Al and Mg-Zn alloys. The second phase was assumed to be Mg₁₇Al₁₂ phase and its initial amount was taken from Mg-3 wt. % Al binary alloy. It should be noted that in the real as cast microstructure of AZ31 (and all AZ alloys), there are also a certain amount of ternary phase (Φ and Γ phases) and binary Mg₂Zn phase along with large amount of Mg₁₇Al₁₂ phase. Unfortunately, because the interdiffusivities of the ternary phases were not known, so it is difficult to do simulation with taking them into account at current stage.

The simulated results for second phase fraction and microsegregation profiles of Al and Zn in Mg for AZ31 at 673 K (400 °C) are shown in Fig. 9.12. In general, the homogenization behavior of AZ31 is similar to Mg-3 wt. % Al and Mg-1.5 wt%. Zn alloy but the dissolution rate of $Mg_{17}Al_{12}$ phase in AZ31 is slightly faster than that in binary Mg-3 wt. % Al alloy due to the ternary effect. The homogenization process of AZ31 comes to equilibrium for both solute (Al and Zn) elements after 8 hrs of annealing at 673 K (400 °C).

The present model is still insufficient to predict the general homogenization process of real Mg alloy. The shortcomings of the present model are no consideration of i) possible precipitation of second phase from supersaturated matrix during the annealing at low temperature, ii) phase transformation of second phase to other intermetallic phases, iii) partial melting at grain boundary due to heavy segregation, and iv) two step approximation (dissolution of second phase

and homogenization of microsegregation in Mg matrix) without 2 or 3 dimension calculation. However, from the practical view point, the present model can give a good description of microstructural change of Mg-Al-Zn alloys during their homogenization process.

9.6. Summary

Annealing experiments for as cast Mg-Al (3, 6 and 9 wt. % Al) and Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) binary alloys were performed at 603 and 673 K (330 and 400 °C) to systematically investigate the dissolution rate of second phase and homogenization of microsegregation of solute Al and Zn in Mg matrix. As cast Mg-Al alloys contained 0.85, 2.82, and 3.49 % of Mg₁₇Al₁₂ phase with 3, 6 and 9 wt.% Al, respectively, and as cast Mg-Zn alloys contained 0.93, 2.49, and 3.16 % of Mg₅₁Zn₂₀ phase with 1.5, 4.0, and 5.5 wt. % Zn, respectively. The Mg-Al alloys and Mg-Zn alloys were homogenized almost completely at 673 K (400 °C) after annealing of 8 hrs and 4 hrs, respectively. When the solute Al and Zn contents are similar in Mg alloy, the dissolution rate of Mg₅₁Zn₂₀ intermetallic phase in Mg-Zn alloys was faster than that of Mg₁₇Al₁₂ phase in Mg-Al alloys at given temperature.

1 dimensional homogenization model based on diffusion simulation with moving boundary between hcp Mg and second phase was proposed to explain the microstructural change of the Mg-Al and Mg-Zn alloys with time. The model is consisted of two step calculations: (*i*) the dissolution of second phase in hcp Mg and (*ii*) the homogenization of microsegregation of solute in hcp Mg. The predicted results from the present homogenization model are in good agreement with the experimental data. The expansion of the model for ternary Mg-Al-Zn system (AZ alloy) was also explained.

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9.8. References

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Table 9.1. Summary of the diffusion coefficients used in the present study.

	Intern		
Interdiffusion coefficient	603 K	673 K	Reference
	D		
$\widetilde{D}_{\mathrm{Mg}_{17}\mathrm{Al}_{12}}$	3.24×10^{-5} ex	[7]	
$\widetilde{D}_{\mathrm{Mg}_{51}\mathrm{Zn}_{20}}$	6.56 ×10 ⁻¹⁴	7.40×10^{-13}	[8]
'			
Impurity diffusion	Mg hcp solid		
coefficient	D	-	
D_{Mg}^{hcp-Mg}	1.75×10^{-4} ex	[19]	
D_{Al}^{hcp-Mg}	7.18×10^{-3} ex	[7]	
D_{Zn}^{hcp-Mg}	4.98×10^{-5} ex	[8]	

The interdiffusion coefficient of $Mg_{51}Zn_{20}$ is determined only at 603 K due to its very small thermal stability range (598 ~ 619 K). Therefore, the diffusivity is assumed to be constant in the present study. R is molar gas constant and T is temperature in Kelvin.



Fig. 9.1. Schematic illustration of as cast ingot from CANMET for present study with thermocouple position: (a) sample from water cooled Cu plate shape mold, and (b) sample from water cooled Cu wedge shape mold.



Fig. 9.2. Schematic illustration of line scanning across grain boundary for Mg-Al and Mg-Zn binary alloys.



(a)



Fig. 9.3. Mg rich side of the equilibrium diagrams: (a) Mg-Al binary system, and (b) Mg-Zn system [9]. Dotted lines represent the alloy compositions and annealing temperatures.



Fig. 9.4. BSE micrographs for as cast and annealed Mg-3 wt. % Al, Mg-6 wt. % Al, and Mg-9 wt. % Al.



(b)

Fig. 9.5. Second phase fraction in Mg-3 wt. % Al, Mg-6 wt. % Al, and Mg-9 wt. % Al alloys: (a) annealed at 603 K (330 °C) and (b) annealed at 673 K (400 °C).



Fig. 9.6. BSE micrograph for as cast and annealed Mg-1.5 wt. % Zn, Mg-4.0 wt. % Zn, and Mg-5.5 wt. % Zn.



(b)

Fig. 9.7. Second phase fraction in binary Mg-1.5 wt. % Zn, Mg-4.0 wt. % Zn, and Mg-5.5 wt. % Zn alloys: (a) annealed at 603 K (330 °C) and (b) annealed at 673 K (400 °C).

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Fig. 9.8. Solute concentration profile across grain boundary in as cast and annealed condition with modeling results: (a) Mg- 3 wt. %Al, (b) Mg- 6 wt. % Al, and (c) Mg- 9 wt. % Al, annealed at 603 K (330 °C), and (d) Mg- 3 wt. %Al, (e) Mg- 6 wt. % Al, and (f) Mg- 9 wt. % Al, annealed at 673 K (400 °C).



Fig. 9.9. Solute concentration profile across grain boundary in as cast and annealed condition with modeling results: (a) Mg-1.5 wt. %Zn, (b) Mg- 4.0 wt. %Zn, and (c) Mg-5.5 wt. %Zn, annealed at 603 K (330 °C), and (d) Mg-1.5 wt. %Zn, (e) Mg- 4.0 wt. %Zn, and (f) Mg-5.5 wt. %Zn, annealed at 673 K (400 °C).



(b)

Fig. 9.10. (a) The modeling result of second phase $(Mg_{17}Al_{12})$ dissolution in hcp Mg at 673 K (400 °C) for binary Mg-9 wt. % Al alloy, and (b) enlarged view of second phase $(Mg_{17}Al_{12})$ region.



Fig. 9.11 Second phase fraction modeling results: (a) Mg-Al after annealed at 603 K (330 °C), (b) Mg-Al after annealed at 673 K (400 °C), (c) Mg-Zn after annealed at 603 K (330 °C), and (d) Mg-Zn after annealed at 673 K (400 °C)



Fig. 9.12. Homogenization modeling results for ternary Mg-3Al-1.5Zn alloy (in wt. %): (a) Changes in second phase fraction at 603 K (330 °C), and 673 K (400 °C), (b) Al solute profile in Mg grain at 673 K (400 °C), and (c) Zn solute profile in Mg grain at 673 K (400 °C).

Chapter-10

Summary and future work

Knowledge on diffusion kinetics is the key to design and optimize high temperature process in materials. Phase transformation, precipitation, homogenization, recrystallization etc. are controlled by diffusion. Therefore diffusion kinetics as well as thermodynamics are the fundamental knowledge for computational materials design and process optimization. Although Mg alloys have been studied actively for the industrial applications, there is lack of diffusion kinetic study for Mg alloys in literature.

The prime interest of this work is to perform a systematic kinetic study on Mg based alloys and build a good diffusion database to develop reliable diffusion simulation software which can predict diffusion processes. In this regard, diffusion couple experiments with Mg single crystal were performed to determine anisotropic solute diffusion coefficients of common alloying elements in hcp Mg. Annealing experiments for as cast Mg alloys were also carried out to investigate the changes in microsegregation and second phase fraction during annealing process.

Diffusion couple experiments with Mg single crystal were performed with Al, Zn, Gd, and Y in a tube furnace under Ar atmosphere. The anisotropic diffusion coefficients of these alloying elements in hcp Mg were experimentally determined for the first time. The interdiffusion coefficients and growth constants of intermetallic phases in the binary Mg systems were also determined. Many of them were determined also for the first time.

According to the experimental results, the anisotropic diffusion coefficient of all solute are larger at lower temperature, but it was not significant in the conventional processing temperature ranges of Mg. The diffusion of the solute along the a-axis (parallel to the basal plane) of Mg is slightly faster than that along the c-axis (perpendicular to the basal plane). The maximum difference between the diffusion coefficients is about $D\perp/D_{\parallel} = 1.3$. On the other hand, the diffusion coefficients of

Al and Zn are similar to the self-diffusion coefficient of Mg, while the diffusion coefficients of REE (Gd and Y) is about one order of magnitude lower than the others.

Grain boundary diffusion of Al in Mg was also investigated using the polycrystalline Mg diffusion couple experiments. The concentration profile of Al along Mg grain boundary was successfully measured by CFE-SEM EDS analyses. The grain boundary diffusion coefficient of Al is found to be dependent on misorientation of grains and is as large as two orders of magnitude higher than volume diffusion of Al.

Annealing experiments with binary Mg-Al (3, 6 and 9 wt. % Al), and Mg-Zn (1.5, 4.0 and 5.5 wt. % Zn) alloys were performed at 603 and 673 K (330 and 400 °C). The dissolution rate of second phase in each binary system was determined depending on solute content and annealing temperature. In addition, the change of microsegregation (inhomogeneity in solute) was also studied with annealing time.

The diffusion simulation model was developed to predict multiphase diffusion simulation for diffusion couple and homogenization of as-cast microstructure. The diffusion simulation model was developed on the fundamental diffusion equations formula using explicit FDM, and was coded in FORTRAN language. The moving boundary feature and composition dependent mobility concept were used in diffusion model. The thermodynamic data were taken from the Facsage FTlite database and all the diffusion coefficient from the present experimental study were also taken into account as thermodynamic and kinetic parameters in the model. The model can successfully reproduce the experimental diffusion couple and homogenization results.

Overall, this present work provides a systematic experimental diffusion study and diffusion database for Mg based alloys. However, there are some limitations of the present study which can be further investigated in future. Firstly, the present study described the technique to determine the diffusion coefficient for binary Mg alloy, but the systems investigated in this study are only limited to Mg-Al, -Zn, -Gd, and -Y. There are many other alloying elements for Mg alloys such as Sn, Mn, Ca, Ce, Nd, Si, Li, Ag, Bi etc. The diffusion coefficient of such alloying elements should be investigated. In the case of Ca and Si, the solubility in hcp Mg is negligible,

so determination Ca and Si diffusion coefficient would be difficult. But, other elements should be studied in future.

The present diffusion simulation code is limited to ternary system. For more versatile applications, the code should be expanded to multi-component system. The other limitation of the present simulation is no nucleation kinetics in the diffusion code, which can be added in future. Technical limitation of the present simulation code is no direct linkage (automatic access) to the thermodynamic database. This should be resolved for the convenience of the diffusion simulation in future.

Chapter-11

Contributions to original knowledge

(1). Anisotropic diffusion coefficients of Al, Zn, Gd, and Y in hcp Mg were determined for the first time using diffusion couple experiment with Mg single crystal. Anisotropic impurity diffusion coefficients of all the solutes (Al, Zn, Gd, and Y) reported in the present study depending on the orientation of hcp Mg crystal were found to be faster along the a-axis (the basal plane) compared to the c-axis (normal to the basal plane). The diffusion coefficient of all the solutes were about 1.3 times faster along the a-axis direction of Mg crystal.

(2). Interdiffusion coefficients and growth constants of all intermetallic phases in Mg-Al, Mg-Zn, Mg-Gd, and Mg-Y systems were determined. Many of them were determined for the first time.

(3). The grain boundary diffusion of Al in Mg was determined quantitatively for the first time and found to be highly dependent on the misorientation angle of adjacent grains. Al grain boundary diffusion was found to be even two orders of magnitudes faster than volume diffusion of Al in Mg grain.

(4) Diffusion simulation models for multiphase diffusion couple and homogenization of as-cast binary Mg alloy were developed. Numerical simulation was done using explicit FDM for diffusion optimization with moving boundary treatment.

(5). Non-stoichiometry of Mg₅Gd, Mg₃Gd, and Mg₂Gd intermediate phases in the Mg-Gd binary system and solubility of Mg in hcp Y in the Mg-Y system in temperature between 700 and 800 K were observed for the first time from the present study. Using new phase diagram data, the thermodynamic modeling of the Mg-Gd and Mg-Y systems were performed.

Chapter-12

Appendix

Original diffusion couple experimental data for Mg-Gd and Mg-Y binary systems

Table 12.1. Summary of the experimental results for Mg single crystal and Gd diffusion couples.

Annealing condition		Length of the Intermetallics layers (µm)									
		Mg	₅ Gd	Mg	₃ Gd	Mg ₂	Gd	Mg	;Gd	Mg ₄ 0	Gd ₆
T (K)	days	Mg single crystal orientation*									
		а	с	a	с	а	с	а	с	а	с
703	3	26.1	25.4	67.8	67.1	46.9	46.1	1.18	1.15	0.52.	0.509
	5	33.2	32.9	85.2	85.6	59.8	60.1	1.52	1.48	0.672	0.657
	7	41.2	40.8	101.3	100.9	72.1	71.5	1.80	1.76	0.795	0.777
723	2	27.2	26.8	78.3	77.9	47.2	46.5	1.22	1.17	0.552	0.521
	3	32.3	31.6	91.2	92.6	54.5	53.8	1.41	1.39	0.664	0.647
	4	38.5	37.6	108	105	64.5	63.4	1.59	1.56	0.786	0.775
743	2	33.2	32.8	84.6	84.1	61.9	60.9	1.42	1.39	0.689	0.669
	3	42.1	41.3	105.6	104.9	74.4	73.7	1.69	1.65	0.874	0.865
	4	46.8	46.2	121.3	120.5	88.8	87.2	1.97	1.93	0.996	0.982

*diffusion along the a-axis and c-axis direction in single crystal hcp Mg

Annealing condition		Length of the Intermetallics layers (µm)							
		Mg ₂	₄ Y ₅	Mg ₂ Y		MgY			
T (K)	davs	Mg single crystal orientation*							
		a	с	а	c	a	с		
	2	56.8	56.3	21.7	21.5	0.681	0672		
723	3	67.7	67.3	25.9	26.2	0.815	0.822		
	4	79.4	78.9	29.7	29.3	0.979	0.978		
	2	69.1	68.8	26.5	25.9	0.926	0.917		
743	3	82.1	81.4	31.5	30.8	1.15	1.14		
	4	92.9	93.1	36.1	35.9	1.35	1.29		
	2	76.9	77.1	35.2	34.6	1.57	1.54		
773	3	86.3	85.7	43.2	42.8	1.98	1.95		
	5	109.2	103.7	55.8	56.1	2.58	2.54		
	2	90.1	89.6	39.3	38.8	2.05	2.01		
803	3	110.2	109.5	47.7	48.3	2.54	2.61		
	5	136.1	135.6	63.6	63.8	3.26	3.18		

Table 12.2. Summary of the experimental results for Mg single crystal and Y diffusion couples.

*diffusion along the a-axis and c-axis direction in single crystal hcp Mg