UNIVERSIDAD POLITÉCNICA DE MADRID

ESCUELA TÉCNICA SUPERIOR DE
INGENIEROS DE CAMINOS, CANALES Y PUERTOS

**High throughput investigation of diffusion
and solid solution hardening
of HCP Mg alloys**

TESIS DOCTORAL

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Ingeniero de Materiales

2019

Departamento de Ciencia de Materiales

Escuela Técnica Superior De Ingenieros de
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Universidad Politécnica de Madrid

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2019

This is not the end, but a new beginning...

Acknowledgements

This doctoral thesis has been carried out with the support of the European Research Council under the European Union's Horizon 2020 research and innovation programme (Advanced Grant VIRMETAL, grant Agreement no. 669141). I also gratefully acknowledge the financial support from China Scholarship Council (Grant no. 201506890002).

During these four years, there are many people who have helped me a lot in different ways. I would like to give my deepest thanks to all of them.

First of all, I would like to express my most sincere gratitude to my supervisors Prof. Javier Llorca and Prof. Yuwen Cui for their constant support, valuable guidance, continuous encouragement and sufficient freedom throughout the course of my PhD. It would have been impossible to success in this challenge without you. You are always incredible people who never hesitate to help me in my work and to teach me how to perform scientific research. Whenever I met problems and felt helpless, you always helped me out patiently. It has been a great honor working with you.

I would also like to extend my deepest appreciation to Dr. Jon Molina-Aldareguía for your tremendous, qualified and friendly support in conducting various experiments, discussion and careful guidance on my work.

My sincere gratitude to Dr. Miguel Monclús for your dedication and support with the nanomechanical testing facilities and to Dr. Miguel Castillo for your valuable help in the TEM characterization and FIB operation. I would also like to sincerely thank Dr. Alberto Parlomales, Dr. Reza Alizadeh, Dr. Raúl Sánchez, Dr. Chuanyun Wang for your invaluable help with my experiments. I am deeply grateful to Dr. Guanglong Xu for your support and guidance in my simulations.

I would also express my deepest gratitude to Rosa María Bazán and Mariana Huerta because of your help for my application of the visa and looking for my apartment when I came here four years ago.

All my colleagues and friends of IMDEA Materials Institute are greatly acknowledged for providing a nice working atmosphere and for your kind help in my work and in my life during this incredible journey of four years. Especially to Nana Chen, Dr. Sha Liu, Dr. Zhilin Liu, Na Li, Dr. Xiangxing Deng, Peikang Xia, Gustavo Esteban, Bárbara Bellón, Dr. Sarra Haouala, Jifeng Li, Xueze Jin, Rudi Maça, Daniel Cíntora-Juárez, Mario Rueda, Marcos Jiménez, Dr. De-Yi Wang, Lu Zhang, Dr. Shuang Hu, Qi Wang, Jing Zhang, Dr. Zhiqi Liu, Dr. Zhi Li, Dr. Yetang Pan, Wei Liu, Dr. Hong Liu and many more. Because of you, life and work are full of fun and happiness.

Last but not least, I would like to give my greatest gratitude to my family for their endless support and encouragement. Special thanks to my beloved husband, Dr. Weisen Zheng. This thesis is dedicated to you with my deepest love.

Jingya Wang

June, 2019

Resumen

El Magnesio es mas ligero de los metales estructurales y se postula como una alternativa en muchas aplicaciones industriales debido a su alta rigidez específica, su gran capacidad de amortiguamiento y su biocompatibilidad junto a su excelente conductividad térmica y eléctrica y su alta reciclabilidad. Sin embargo, algunas cuestiones impiden su aplicación en distintos campos en elementos estructurales. Entre ellas cabe citar su limitada ductilidad y resistencia mecánica a temperatura ambiente que provienen de la anisotropía en las propiedades mecánicas y de los valores reducidos de la tensión crítica resuelta para inducir el movimiento de las dislocaciones en el plano basal y para el maclado. Estas limitaciones podrían superarse mediante la aleación con otros elementos metálicos y esta tesis está dirigida a proporcionar un conocimiento mas profundo de la relación composición-estructura-propiedades mecánicas en aleaciones de Mg para aplicaciones estructurales.

Con este fin, la tesis comienza con un análisis detallado de la cinética de difusión en aleaciones hexagonales del sistema Mg-Al-Zn. En particular, los parámetros de movilidad atómica se optimizaron a partir de una evaluación de la información experimental en la literatura de los sistemas Mg-Al, Mg-Zn y Mg-Al-Zn junto con las correspondientes bases de datos termodinámicas. El conjunto de parámetros de movilidad atómica optimizados es capaz de predecir la cinética de difusión en pares de difusión binarios y ternarios.

Además, se ha desarrollado una nueva estrategia experimental de alto rendimiento basada en pares de difusión para determinar los coeficientes de difusión en función de la orientación en aleaciones de Mg-Al. Como resultado se ha obtenido una expresión explícita de los coeficientes de difusión del sistema hexagonal Mg-Al en función del

contenido de Al, la orientación del grano y la temperatura. Estos pares de difusión, en combinación con ensayos mecánicos de micropilares, se utilizaron para estimar la influencia del contenido de Al y la temperatura en la tensión crítica resuelta para mover dislocaciones en los planos basal y piramidal y para producir el maclado. Estos nuevos resultados se compararon con estimaciones teóricas basadas en cálculos de primeros principios y se concluyó que la anisotropía plástica del Mg aumenta con el contenido de Al. Finalmente, las nuevas estrategias de alta rendimiento desarrolladas en esta tesis se pueden extrapolar fácilmente a otras aleaciones metálicas hexagonales.

Abstract

Magnesium, the lightest structural metal, is a potential alternative as weight-saving material for many industrial applications due to high specific-stiffness, superior damping capacity and biocompatibility together with excellent electrical and thermal conductivity and recyclability. However, some key issues limit its widespread application as a structural material, such as the reduced ductility and low strength at room temperature, resulting from the mechanical anisotropy and low critical resolved shear stress for basal slip and twinning. These limitations may be overcome by the addition of alloying elements and this thesis was aimed at providing a deeper understanding of the composition-microstructure-mechanical properties link in Mg alloys for structural applications.

To this end, a complete assessment of the kinetic database of the hcp Mg-Al-Zn system was performed. In particular, the atomic mobility parameters were optimized based on the evaluation of the experimental diffusion data available in the literature for the Mg-Al, Mg-Zn and Mg-Al-Zn systems, in combination with the available thermodynamic databases. The optimized set of atomic mobility parameters could successfully predict the diffusion behavior for binary and ternary diffusion couple.

In addition, a novel high-throughput experimental approach was developed to investigate the anisotropic interdiffusion behavior in Mg-Al alloys by means of diffusion couples and an explicit comprehensive expression of the interdiffusion coefficients of the hcp Mg-Al alloys as a function of Al content, grain orientation and temperature was determined. Moreover, the diffusion couples in combination with micropillar compression tests, were used to estimate the influence of solute content and temperature on the critical resolved shear stress for the basal slip, twinning and

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CHAPTER 1

Introduction

1.1 Mg and Mg alloys

Mg is an alkaline-earth metal that belongs to the Group II of the periodic table. Mg is the 4th more abundant element on earth and comprises 2.7% of the earth's crust. It is the lightest structural metals (density of 1.74 g/cm³), and Mg and its alloys have attracted significant interest recently for structural applications in automotive, aerospace, electronics, and biomedical sectors [1-8]. Mg and its alloys attracted significant interest recently for structural applications in automotive, aerospace, electronics, and biomedical sectors due to their low density, high specific-stiffness, superior damping capacity and biocompatibility excellent electrical and thermal conductivity and recyclability [1-3].

From the structural viewpoint, the main limitations of Mg are the limited strength,

1.2 Structure and properties of Mg

reduced ductility and formability at ambient temperature as well as the poor corrosion resistance [1,2]. As in most of metallic materials, these properties can be improved by means of alloying to achieve solid solution and precipitation hardening, as well as by modification of the microstructure by means of thermo-mechanical treatments. For instance, addition of Al and Zn can significantly increase the strength, as well as improve the castability of Mg alloys. Ca additions are known to improve the creep resistance by hindering grain boundary sliding at elevated temperatures [3] while Zr is able to limit grain growth in Mg alloys processed by casting [4]. Thus, understanding and exploring the effect of alloying elements on the microstructure and mechanical properties of Mg is an important task.

1.2 Structure and properties of Mg

1.2.1 Crystallography of Mg

Pure Mg presents the hexagonal close-packed (HCP) crystallographic structure under atmospheric pressure [5]. The atomic occupancies of the hcp Mg unit cell are illustrated in Figure 1.1, along with its principal planes and directions. The unit cell contains three layers of atoms following the stacking sequence of ABABABAB... along the c direction (Figure 1.1). The primitive hexagonal unit cell contains 3 axes ($a_1 = a_2 \neq c$) which form angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The lattice parameters a and c for pure Mg at ambient temperature are $a = 0.32092$ nm and $c = 0.52105$ nm with $c/a = 1.6236$, which is close the ideal ratio $\sqrt{8/3}=1.633$.

Figure 1.1 Schematic of the hcp crystallographic unit cell.

1.2.2 Physical and mechanical properties

The most relevant physical and mechanical properties of Mg are depicted in Table 1.1. The melting and boiling points for Mg are low, 650 °C and 1110 °C, respectively, and these limit its application at elevated temperature.

Table 1.1 Physical properties of magnesium.

Property	Value	Reference
Density	1.74 g/cm ³	[5]
Melting point	650 °C	[6]
Boiling point	1110 °C	[6]
Coefficient of thermal expansion	25.5 10 ⁶ °C ⁻¹	[6]

1.2 Structure and properties of Mg

1.2.3 Elastic deformation

Because of the hexagonal HCP structure, the elastic deformation of Mg single crystals is characterized by 5 independent elastic constants [7], that can be found in Table 1.2.

Table 1.2 Elastic constants (GPa) for pure Mg single crystal at 300 K.

C11	C12	C13	C33	C44
59.4	25.6	21.4	61.6	16.4

It is interesting to notice that the elastic deformation of Mg is rather isotropic and fairly independent of the crystal orientation.

1.2.4 Plastic deformation mechanisms

Dislocation slip

Dislocation slip is the most frequent plastic deformation mechanisms in crystalline materials. In the case of metallic materials, the critical resolved shear stress (CRSS) that needs to activate dislocation slip is minimum in the planes with the highest packing density and along the directions with the shortest Burgers vector [8]. In the case of Mg, plastic deformation by dislocation is mainly dominated by four slip systems, namely basal, prismatic, pyramidal I and pyramidal II slip systems, as schematically shown in Figure 1.2. The basal, prismatic and pyramidal I slip systems have a $\langle a \rangle$ Burgers vector and dislocations can glide on these planes along the $\langle a \rangle$ direction, whereas the Burgers vectors of pyramidal I and pyramidal II slip planes are oriented along the $\langle c+a \rangle$ direction.

Figure 1.2 Slip systems in hcp Mg: (a) basal slip; (b) prismatic slip; (c) pyramidal I slip with $\langle a \rangle$ Burgers vector; (d) pyramidal I with $\langle a+c \rangle$ Burgers vector; (e) pyramidal II slip. The slip planes are shaded, while the arrows stand for the Burgers vector.

The CRSS to activate dislocation slip in the different slip systems of Mg have been measured as a function of temperature [9–18] and they are compared in Figure 1.3. It is worth noting that the basal slip takes place at very low values of the CRSS at ambient temperature (~ 0.5 MPa [14–16]) as compared with prismatic (~ 39 MPa [17]) and pyramidal slip (~ 80 MPa [18]). Thus, basal slip becomes the dominant slip system during the deformation of Mg and is partially responsible for the limited yield strength of this metal. The localization of the deformation along the basal plane leads to crack formation and is negative from the viewpoint of the ductility and formability of Mg and Mg alloys. Moreover, plastic deformation of polycrystals can be only accommodated by five independent slip systems according to the Taylor criterion [19,20]. The Burgers vector of basal and prismatic dislocations is parallel to $\langle a \rangle$ and

1.2 Structure and properties of Mg

they can only provide four independent slip systems [21,22]. Thus, pyramidal slip with $\langle c+a \rangle$ dislocations is expected to provide additional independent slip system but the activation of this system requires very high CRSS at ambient temperature.

Figure 1.3 CRSS for the different slip and twin systems of pure Mg as a function of temperature [9–13].

Twinning

Twinning is another important plastic deformation mechanism in Mg and its alloys as well as of many other low symmetry crystals. During twinning, the original (parent) lattice is re-oriented by atom displacements which are equivalent to a simple shear of the lattice points or of some integral fraction of these points. The twinned and parent regions of the crystal are related by a reflection in some plane (the twin plane) and the twinning systems in each crystal are defined by the twin plane and the twin direction as well as by the shear deformation that is accommodated in the twin direction. It should be noted that twinning is a polar mechanism that only occurs when the shear deformation is applied in the appropriate direction so the twinned region has a mirror symmetry with the parent region across the twin plane [23].

1.2 Structure and properties of Mg

Three different twinning systems have identified in Mg and they are shown in Figure 1.4, in which the twin plane and the twin direction are indicated [24]. Tensile twinning is activated by stress states that lead to an extension of the c axis of the HCP Mg lattice, while the compression twins are triggered by the stress states that promote a contraction of the crystal along the c axis. All of them can accommodate plastic deformation along the $\langle c \rangle$ axis of the HCP Mg lattice and thus provide the fifth independent system necessary to accommodate plastic deformation of polycrystals. As a result, twinning strongly affects the mechanical behavior of Mg alloys, including yielding [25], work hardening [26,27], ductility [28] and dynamic recrystallization [29].

Figure 1.4 Twinning systems in Mg, showing the twin plane (shaded) and the twin direction.

The accommodation of plastic deformation by twinning is a process that requires two steps: twin nucleation and twin growth (thickening). Twin nucleation is heterogeneous and takes place in regions with large stress concentrations in the microstructure, such as grain boundaries [23,30]. Several theories were proposed in the past for twin nucleation, including the pole mechanism of Thompson and Millard [31], the slip dislocation dissociation mechanism of Mendelson [32] and the disconnection mechanism proposed by Serra, Bacon and Pond [33–36]. Later, a zonal-twinning mechanism was proposed by Wang [37,38] through the atomistic simulations, using density function theory, in which a stable twin nucleus was created

1.2 Structure and properties of Mg

by simultaneous glide of a zonal dislocation consisting of partial dislocation and multiple twinning dislocations. Regarding the twin growth, it is generally accepted that twin thickening is mediated by the glide of twinning dislocations along the twin planes [33], and such migration is controlled by the resolved shear stress on the twin plane and direction.

It is generally assumed that twin activation is triggered by the CRSS on the twin plane along the twin direction. According to this criterion, the CRSS for the different twin systems in Mg have been measured and they are depicted in Figure 1.3 as a function of temperature [9,11,12]. These results show that the CRSS for the compression twin systems are much higher than those for tensile twinning and, in fact, they are rarely found in Mg and Mg alloys. On the contrary, the CRSS for tensile twinning at ambient temperature of ($\sim 12\text{MPa}$ [39]) is much lower than the CRSS for pyramidal slip and provides the fifth independent deformation system to accommodate plastic deformation of Mg polycrystals. Thus, basal slip and tensile twinning become the dominant deformation mechanisms in Mg polycrystals up to $200\text{ }^{\circ}\text{C}$ – $250\text{ }^{\circ}\text{C}$. Thus, twinning plays a critical role in the plastic deformation of Mg, strongly influencing the mechanical behavior of Mg alloys. Tensile twinning in Mg is associated to a shear strain of 12.9% and leads to a rotation of the c axis of the lattice of 87.3° .

Anisotropic plastic deformation

Plastic deformation of Mg polycrystals mainly takes place by basal slip and twinning, that are activated for low values of the CRSS. It should be noted, however, the twinning is a polar mechanisms that only develops when the applied shear stress favors the extension of the c axis (in the case of $\{01\bar{1}2\}\langle 0\bar{1}11\rangle$ tensile twinning). This leads to a marked anisotropy in the plastic deformation in the case of textured polycrystal, as shown in Figure 1.5 for a polycrystalline AZ31 Mg alloy tested at room

1.2 Structure and properties of Mg

temperature. The alloy was processed in the form of a 25.4 mm thick plate by hot rolling. The average grain size was 25 μm and the pole figure of the as-rolled material is plotted in Figure 1.5a. It shows the strong basal texture typical of rolled Mg alloys, with c axis parallel to the normal direction (ND). Also, the spread prismatic poles appear along the rolling (RD) and transverse (TD) directions. Specimens for tension and compression tests were extracted for the rolled plate in different orientations, as indicated in Figure 1.5b and the corresponding stress-strain curves in tension and compression in the ND, and in tension in the RD directions are plotted in Figure 1.5c together with the ones corresponding to the tensile tests in the RD-ND plane at 45° from both orientations [40]. These curves show the strong plastic anisotropy of Mg alloys, which is triggered by the limited number of slip systems and by the polar nature of extension twinning, that is only activated when deformation leads to an extension of the c axis. As a result, tensile twinning cannot be activated when the specimen is loaded in tension along the RD or in compression along ND and the high CRSS for pyramidal slip leads to a very high value of the yield strength. On the contrary, tensile twinning occurs at low stress in the samples loaded in tension along ND or in the RD-ND plane at 45° from both orientations, leading to a much lower yield strength. Thus, deformation of wrought Mg alloys is markedly dependent on the orientation, and different slip systems (and in different order) are activated as a function of the loading direction (either tension or compression).

The plastic anisotropy in the mechanical response of Mg and Mg alloys has very negative effects on the formability and ductility of Mg alloys at ambient temperature. Nevertheless, it disappears at high temperature because the CRSS for basal slip and tensile twinning is not affected by the temperature but those of the hard deformation modes decrease rapidly as the temperature increases (Figure 1.3) [9–13]. So, plastic anisotropy disappears for temperatures above 250 °C–300 °C. And thus, rolling and extrusion becomes possible to manufacture wrought products.

1.2 Structure and properties of Mg

Figure 1.5 (a) Pole figures of rolled AZ31 Mg alloy. (b) Schematic of the loading directions for the mechanical tests of the rolled plate of AZ31 Mg alloy. (c) Stress-strain curves of the rolled AZ31 Mg alloy along different orientations, showing the plastic anisotropy [40].

Obviously, the anisotropy of the plastic deformation in Mg alloys can be reduced by increasing the CRSS to promote basal slip and twinning. Moreover, these changes will increase the overall yield strength of the Mg alloys because basal slip and twinning are the softest deformation mechanisms. This can be achieved through several processes including precipitation, reduction of grain size and solid solution. Basal slip can be significantly strengthened by solid solution as it has been confirmed by many experimental studies with different solute atoms (Zn, Cd, Sn, In, Al, Pb, Bi, Nd, Y and Dy) [41–48]. For instance, the CRSS for basal slip showed an increase up to 2.5 MPa and 2 MPa with the addition of 1.6 at.%Al and 0.5 at.%Zn according to tensile tests in the single crystals of Mg-Al [42] and Mg-Zn [44] alloys, respectively. The solid solution strengthening of basal slip due to Y and Dy was measured through the compression tests in single crystals, and the CRSS increased up to ~10 MPa and ~5 MPa with the addition of 1.0 at.%Y and 0.5 at.%Dy, respectively [47].

Regarding solid solution strengthening of tensile twinning, it has been reported that Y, Zr, Nd and Li increase the CRSS for twinning [49–52], while the effect of Zn is negligible [53,54]. For instance, the CRSS value to activate tensile twinning in Mg was increased up to ~100 MPa by the addition of 10 at.%Y [50], while 5 wt.%Li improved the CRSS for twinning up to ~ 25 MPa [52]. However, these analyses were carried out in polycrystalline samples and the effect of the alloying elements on the CRSS for twinning was estimated indirectly after it was isolated from other hardening mechanisms (grain boundaries, latent hardening and the influence of the solute atoms on basal, prismatic and pyramidal slip). Moreover, these strategies based on tests in polycrystals cannot distinguish between the effect of solute atoms on the CRSS for twin nucleation and growth. Thus, reliable experimental data of the influence of solid solution on the CRSS for basal slip and tensile twinning are scarce because mechanical testing of single crystals is very time and cost consuming due to the fact that single crystals with various solute contents have to be manufactured.

1.3 Diffusion behavior in Mg

Taking into account the industrial interest in Mg alloys and the limitations in the mechanical properties from the viewpoint of strength and formability, it is important to develop a fundamental understanding of the chemical composition-microstructure-mechanical properties link. In particular, tailoring the microstructure of metallic materials by means of alloying is a well-known strategy to improve the mechanical properties.

One critical factor that determines the composition-microstructure-properties in alloys is the diffusion behavior of the alloying elements. Obviously, diffusion is critical in many processes such as solidification, segregation, precipitation and phase

1.3 Diffusion behavior in Mg

transformation and it has been integrated into the materials design approaches to determine many process parameters during the metallurgical processes, such as rolling, casting, forging, etc. Furthermore, diffusion behavior also is important to understand creep resistance [55,56], dynamic strain aging [57] and plastic instabilities [58]. Therefore, an accurate knowledge of the solute diffusion coefficients in Mg is critical for the development of new Mg alloys with improved properties. In order to ascertain the diffusion behavior, the CALPHAD methodology, based on the diffusion controlled transformation package (DICTRA), is employed in this work.

1.3.1 Bulk diffusion behavior

The information of experimental bulk diffusion data for Mg alloys is very scarce due to the experimental difficulties associated with melting high purity Mg alloys because of its high vapor pressure. The self-diffusion coefficient of pure Mg was initially measured in extruded polycrystalline Mg alloy by Shewmon [59] in the temperature range from 468 °C to 627 °C. Subsequently, Kulkarni et al. [60] used secondary ion mass spectrometry to extract concentration profiles of the ^{25}Mg radioactive isotope to determine the tracer diffusivity in pure Mg. Regarding the impurity diffusion coefficients, they were experimentally measured using three major protocols, including the liquid-solid diffusion couple (LSDC) method [61,62], the solid-solid diffusion couple method [63–67] and radioactive tracers [68–75] for various solutes, including Al, Zn, Cu, Mn, Ag, Sn, Y, and Nd. The concentration profiles were obtained through residual activity [70], secondary ion mass spectrometry (SIMS) [76] analysis or serial sectioning methods [70].

Interdiffusion coefficients in Mg were widely studied using the diffusion-couple technique for the single HCP Mg phase [65,66,77] or for intermetallic phases of Mg-X (X=Al, Zn, Gd, Y and Nd) [63,64,67,78]. In the case of ternary systems, interdiffusion

coefficients were only investigated in the Mg-Al-Zn system via the diffusion-couple method [79]. Based on the critical assessment of the limited available experimental information, a database of atomic mobility parameters for HCP Mg alloys binary systems was developed by Bryan [80]. However, there is not yet any available atomic mobility database for the HCP Mg alloys ternary systems.

1.3.2 Anisotropic diffusion behavior

The majority of investigations on the bulk diffusion behavior in Mg alloys mentioned above was performed in polycrystalline Mg or Mg alloys. The diffusion coefficients obtained with those strategies are influenced by the contribution from all grains with different orientations and represent effective average diffusion coefficients but they not provide information about the anisotropy of the diffusion processes. Indeed, the diffusion behavior is considered to be anisotropic in many metals with hcp crystal structure, such as α -Ti [81], α -Zr [82], α -Hf [83], Zn [84–86], Cd [87] and Mg [88,89], which means the diffusion coefficients vary with the grain orientation. This anisotropy has root in the hcp lattice, which leads to two different solute jumps, one within the basal plane (A jumps) and another between adjacent basal planes (B jumps) [90–92], as illustrated in Figure 1.6. The solute jumps within the basal plane are expected to be identical in all directions. Hence, the diffusion coefficient tensor is determined by two different diffusion coefficients. $D_{\perp}$ results from the A jumps along the basal plane with a contribution from the B jumps while $D_{\parallel}$ (parallel to the c axis) only depends on the B jumps only.

1.3 Diffusion behavior in Mg

Figure 1.6 Different diffusion jumps in a hcp lattice: jump A within the basal plane and jump B between adjacent basal planes. The diffusion coefficient $D_{\perp}$ depends on the jump A with partial contributions of the jump B, while only jump B contributes to the diffusion coefficient $D_{\parallel}$.

Current precise measurements of the anisotropic self-diffusion or impurity diffusion coefficients largely rely on the use of the radioactive tracers, which is tedious and confines to a one-composition per measurement. More importantly, it is inapplicable to explore the anisotropic interdiffusion behavior or extract interdiffusion coefficients because of the technical difficulties associated with the introduction of the composition gradient. There are increasing efforts to utilize the single crystal or the bi-crystal end-member of the diffusion-couple to determine the anisotropic diffusion coefficients as a function of the grain orientation. Nevertheless, only the impurity diffusion information at the composition close to the terminal end-members has been obtained so far, and the diffusion data are confined to one or two associated orientations. Meanwhile, the diffusion modeling remains challenging to study the complex interdiffusion in binary or higher order hcp alloys. In consequence, the effect of grain orientation on the anisotropic interdiffusion diffusion in hcp Mg alloys is still missing and a robust approach is required that could to explore efficiently the anisotropic interdiffusion behavior to extract essential diffusion data as a function of the grain orientation.

1.4 Objectives

This thesis aimed at providing reliable information about the anisotropic interdiffusion coefficients through the development of high-throughput experimental techniques based on diffusion-couples. Moreover, diffusion couples in combination with novel micromechanical testing based on micropillar compression tests will be used to determine the effect of solute atoms on the CRSS for basal slip and twinning. The strategies presented in the thesis will be applied to Mg-Al, Mg-Zn and Mg-Al-Zn alloys but they can be readily extended to any other system. The experimental data obtained through these techniques will be very valuable to develop a precise picture of the composition-microstructure-mechanical properties link in Mg alloys for structural applications.

In particular, the objectives of this thesis can be divided into three:

- I) Perform a complete assessment of the kinetic database of hcp Mg-Al-Zn system. In particular, the atomic mobility parameters were optimized based on the evaluation of the experimental diffusion data in the literature for the Mg-Al, Mg-Zn and Mg-Al-Zn systems, in combination with the available thermodynamic databases. The optimized set of atomic mobility parameters could successfully predict the diffusion behavior for binary and ternary diffusion couple.
- II) Develop a novel, high-throughput experiment approach to investigate the anisotropic interdiffusion behavior in Mg-Al alloys. An explicit comprehensive expression of the interdiffusion coefficients of the hcp Mg-Al alloys as a function of Al content, grain orientation and temperature was determined in this work. These results enrich the experimental data and observations, and improve the understanding of the anisotropic diffusion in the hexagonal structure materials.

1.4 Objectives

- III) Develop a novel high-throughput experimental methodology based on diffusion-couples and micropillar compression tests to estimate the influence of solute content and temperature on the CRSS values for the basal slip and twinning in Mg alloys. These results were new and were compared with recent theoretical estimations based on first-principle calculations.

The thesis is divided into 7 chapters. The manufacturing process of the Mg alloys and the experimental techniques are presented in Chapter 2, including the diffusion couple preparation, the microstructural characterization techniques as well as the micromechanical testing techniques. Chapter 3 focus on the assessment of the atomic mobility parameters for the hcp Mg-Al-Zn ternary alloys to establish the complete kinetic database for this system. The anisotropic interdiffusion behavior for hcp Mg-Al alloys is presented in Chapter 4 to extract the anisotropic interdiffusion coefficients as a function of grain orientation, alloy content and temperature. Chapter 5 analyzes the effect of Al content and temperature on the CRSS values of basal slip by means of diffusion couples and micropillar compression tests, while Chapter 6 studies the solid solution hardening on the twin nucleation and growth process in Mg using the same methodology. Finally, the main conclusions and the suggestions for the future work are summarized in Chapter 7.

CHAPTER 2

Materials and experimental techniques

This thesis is focused on the analysis of anisotropic diffusion behavior and the influence of the solid solute content, crystal orientation and temperature on the deformation mechanisms in hcp Mg-Al alloys. The investigation was achieved by mean of a high-throughput technique based on the fabrication of diffusion couples to determine the anisotropic diffusion behavior in grains with different solute content and orientation within the diffusion region. Moreover, micromechanical characterization techniques (i.e. micropillar compression) were performed within the diffusion region to determine the mechanical properties of single crystals with different solute content and orientation as a function of temperature. This chapter introduces the material processing techniques used to prepare the Mg-Al diffusion couples as well as the subsequent microstructural and mechanical characterization techniques.

2.1 Materials processing

2.1 Materials processing

The polycrystalline diffusion couples were fabricated as indicated in the schematic flow chart in Figure 2.1. The pure Mg and Mg-9 at.%Al alloys were melted and cast in an Induction furnace (VSG 002 DS, PVA TePla) (Figure 2.2a) using high-purity Mg (99.99 wt.%) and Al (99.99 wt.%) pellets under a protective Ar atmosphere to avoid oxidation. During melting, the power was increased at a rate of 0.1 kW/minute until 3.0 kW to ensure a steady heating process, and the melt was mixed thoroughly for five minutes before casting. The ingots were homogenized under an Ar atmosphere in quartz capsules at 673 K for 15 days to ensure the homogeneity of the composition and to obtain the large grains (> 1 mm). They were then cut into discs of 12 mm in diameter and 7.5 mm in length, which were grinded following the standard metallographic process to from 320 grit to 2000 grit and then polished with 3 μm and 0.25 μm diamond paste to obtain a mirror-like surface.

Figure 2.1 Schematic of the procedure for the fabrication of the Mg-Al diffusion couples.

The Mg/Mg-9 at.%Al diffusion couples were prepared by diffusion bonding of the pure Mg and the alloy discs under a compressive load of 800 N for 1 h at 673 K under

2.2 Metallographic sample preparation

vacuum in a Gleeble 3800 thermo-mechanical simulator (Figure 2.2b). The diffusion couples were annealed at 673 K (400 °C) for 352 h and at 723 K (450 °C) for 215 h in quartz capsules under the protection of Ar atmosphere, followed by quenching in water. The times and temperatures ensured that the diffusion reached a steady state and the thermal stresses were fully released.

Figure 2.2 (a) Induction furnace used for melting and casting; (b) Gleeble 3800 thermomechanical simulator used for assembling the diffusion couples.

2.2 Metallographic sample preparation

Several parallelepipedal specimens of $7 \times 7 \times 2 \text{ mm}^3$ were cut along the direction perpendicular to the contact plane from the as-fabricated diffusion couples using a wire cutting machine at a low cutting speed to avoid the surface deformation. The surface of interest was manually ground using the abrasive SiC papers with the grit size of 320, 600, 1200 and 2000 to ensure that the scratches obtained from each step were totally removed. The samples were cleaned carefully using absolute ethanol to eliminate contamination.

Afterwards, the surface was manually polished using a conventional polishing machine to obtain a mirror-like flat surface using the following procedure. Firstly, the

2.3 Microstructural characterization techniques

surface was polished using a MD-Mol cloth with 3 μm diamond paste. Then, a 0.25 μm diamond paste was introduced in the MD-Nap cloth to remove the scratches resulting from the mechanical polishing. Finally, the sample was carefully rubbed during ~50 s against a MD-Chem cloth that has been pre-impregnated with a solution of 75 ml ethylene glycol, 24 ml of distilled water and 1 ml of nitric acid. The microstructural features, such as grain boundaries, were clearly revealed and the deformation resulted from the mechanical polishing process was totally relieved.

2.3 Microstructural characterization techniques

The microstructure of the diffusion couples was systematically characterised using scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and electron backscatter diffraction (EBSD). And after the micromechanical tests, the deformed micropillars were also characterized by SEM, transmission EBSD (*t*-EBSD) and TEM.

2.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electron microscope to acquire an image using the beam of accelerated electrons. The scanning electron microscopy (SEM) mainly consists of the electron gun, anode, electromagnetic lenses, scanning coils, signals detector and display devices, which are held in the vacuum. The beam of high-energy electrons, with an energy ranging from 0.2 keV to 40 keV, is produced by the electron gun at the top of the microscope, accelerates down and passes through a series of electromagnetic lenses to produce a focused beam with a spot size of ~0.4 nm to 5 nm towards to the sample surface.

2.3 Microstructural characterization techniques

The position of the electron beam on the sample area of interest is controlled by the scan coils situated above the objective lens. This beam, rastering or scanning, enables information about a defined area on the sample to be collected. When the beam of high-energy electrons hits the sample surface, the interaction between the beam and the sample surface produces four main different emission signals, including the secondary electrons (SE), backscattered electrons (BSE), characteristic X-rays and diffracted backscattered electrons, which are then collected by the suitable detectors and sent to a screen, forming the final images. The secondary electrons (SE) are emitted from the region close to the sample surface, ~5-20 nm, efficiently revealing the microstructural topography of the sample surface. The characteristic X-rays are generated in deeper region below the sample surface and retain larger interaction volume. They are associated with the atomic number, characteristic energy and characteristic wave lengths, and mainly used to provide the chemical composition analysis. The backscattered electrons (BSE) are intermediate case and they mainly interact with the atomic nucleus of the atoms, Thus, they provide electron images with the information relevant to the atomic structure and composition of the sample.

In this work, SE imaging was employed to characterize the topography of the surface of the diffusion region in the diffusion couples and the micropillar surfaces before and after deformation. The characterization was carried out in a Helios NanoLabTM DualBeamTM 600i microscope (FEI) equipped with a field-emission electron gun and a focused ion beam (FIB). BSE imaging was used to characterize the rough chemical composition of the diffusion region in the diffusion couples, which was measured precisely using a JEOL Superprobe JXA-8900M.

2.3.2 Electron probe microanalysis (EPMA)

Electron probe microanalysis (EPMA) is an efficient non-destructive technique to

2.3 Microstructural characterization techniques

determine the chemical composition of the small regions of material from the characteristic X-rays emitted by the interaction between the high-energy electrons of the beam and the sample surface. An electron is ejected by the inelastic collisions of the accelerated incident electrons with the electrons in the inner shell of an atom. Then, another electron from an outer-shell at a higher energy level comes down to take the place of the ejected electron. This movement between energy levels is accompanied by the emission of an X-ray radiation with a wavelength that is equivalent to the energy difference, which is unique to the specific element.

EPMA is carried out in a SEM, equipped with a wavelength dispersive X-ray spectrometer (WDS). The electron microprobe uses Wavelength Dispersive Spectroscopy for precise quantitative chemical analysis. WDS provides higher accuracy (± 0.5 wt. %) than (EDS) (± 1 wt. %) [98]. In this work, EPMA was carried out in a JEOL Superprobe JXA-8900, equipped with Wavelength Dispersive Spectroscopy (WDS), located in Universidad Complutense de Madrid, Spain. The JXA-8900 instrument is equipped with 5 wavelength dispersive X-ray spectrometers and one energy dispersive X-ray spectrometer. This combination can be used to simultaneously analyze up to 13 elements plus and collect image signals from BSE and SE detectors. It can detect elements ranging from Be to U and the detectable wavelength ranges from 0.087 to 9.3 nm. This technique was used to analyze the chemical composition in the diffusion region and provide the composition profiles of the diffusion couples along lines perpendicular to the diffusion interface. The spatial resolution of the technique is 1 μm .

2.3.3 Electron backscatter diffraction (EBSD)

EBSD is a SEM-based technique to provide information about the crystallographic orientation of the sample. EBSD is based on the acquisition and analysis of Kikuchi

2.3 Microstructural characterization techniques

diffraction patterns from the sample surface in a SEM to obtain the crystallographic information. A well-polished, flat sample is placed in the SEM, inclined by 20° with respect to the incident electron beam, in order to reduce the energy loss during the elastic scattering. A stationary electron beam, coming from the electron gun, interacts with the sample surface. The BSE are diffracted at specific atomic planes within the probe volume and form a set of paired large angle cones corresponding to each diffraction plane. These cones are detected when impinge on a flat phosphor screen of the detector and generate visible lines, called Kikuchi bands. The Kikuchi bands are evaluated and indexed automatically by the specialised computer software and provide the crystallographic orientation.

In this work, the EBSD characterization was employed to determine the grain orientation within the different grains in the diffusion couples. This analysis was carried out in Helios NanoLabTM DualBeamTM 600i microscope (FEI) equipped with an Oxford Instruments NordlysNano EBSD. The AZtec system was employed to analyze the diffracted patterns and the CHANNEL5 software was used to determine the crystallographic orientation.

2.3.4 Transmission Kikuchi diffraction (TKD)

Transmission Kikuchi diffraction (also denominated transmission-EBSD, *t*-EBSD) in the scanning electron microscope (SEM) is a novel characterization technique to acquire the crystallographic information of bulk and nanostructured materials by detecting the transmitted electrons using the conventional EBSD equipment. *t*-EBSD mainly involves the analysis of samples (thickness of around 150 nm) that are transparent to electrons and has a higher spatial resolution (ranging from 2 to 10 nm) than the conventional EBSD.

This technique is a modification of the existing EBSD methods in which the beam

2.3 Microstructural characterization techniques

passes through the sample, rather than reflecting off the surface of the tilted sample. The diffraction patterns presented in *t*-EBSD very closely resemble EBSD patterns, but are formed in transmission rather than by backscattering. The sample is mounted on a flat stage tilted 20° from the horizontal direction. The tilted 20° sample stage ensures electrons that transmit through the sample and undergoes Kikuchi diffraction to be collected by the EBSD detector, and eliminates the problems associated with backscattered electrons scattering from the stage and affecting the *t*-EBSD pattern quality. The sample is positioned at a working distance of 5 mm. The EBSD detector with the phosphor screen, as for the conventional EBSD, is employed to detect and image the transmission Kikuchi patterns, which are analyzed using standard EBSD processing software, CHANNEL5 software from Oxford Instruments.

In this work, the *t*-EBSD characterization was mainly used to determine the deformation mechanism of the deformed micropillars, including the determination of crystal orientation and the presence of twin boundaries. It was carried out in a Helios NanoLabTM DualBeamTM 600i microscope (FEI) equipped with an Oxford Instruments NordlysNano electron backscatter detector (EBSD) using the pre-tilted 20° sample stage. The AZtec system was employed to analyze the diffracted patterns and the CHANNEL5 software were used to extract information about the crystallographic orientation.

2.3.5 Transmission electron microscopy (TEM)

Transmission electron microscope (TEM) is another powerful imaging tool that can provide high resolution images associated with the crystal structure, defects (such as dislocations, stacking fault, interfaces, grain boundaries and twin boundaries, etc.) as well as chemical composition. The TEM consists of three main components: illumination source, electron lens and detectors. A high energy beam of electrons,

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with the energy ranging from 100 keV to 400 keV, is generated in the electron gun and then is converged to a small, thin and coherent beam, with the spot size of 1~5 nm, by passing through a set of condenser lenses and apertures. Afterwards, it is accelerated directly down and transmitted through the sample surface through a series of electromagnetic lenses, including objective lens, intermediate lenses and projection lens. This transmitted portion is focused and form an image on the fluorescent screen, a photographic film or a charge-coupled device (CCD) camera.

The incident electrons transmit through the sample and split into direct beam, which undergoes the inelastic scattering without changing the incident direction, and diffracted beam, which is elastic scattered and diffracted by the lattice planes of the samples based on Bragg's law and thus changes the directions. There are two main different operation modes in the TEM, imaging mode and diffraction mode. In the imaging mode, the objective aperture is inserted in a back focal plane (BFP) of the objective lens, which is utilized to select the imaging beam to form the diffraction contrast. If the direct beam is selected by the objective apertures (the remaining signal is blocked), the bright field image (BF image) is acquired. If we allow the signal from the diffracted beam, the dark field image (DF image) is received. Then, the selected signal is magnified and projected on a screen (or on a camera) with the help of the Intermediate and Projector lenses. The bright-field (BF) and dark-field (DF) imaging efficiently provide the information of the sample surface morphology and defect structures. In the diffraction mode, the diffraction patterns formed in the back focal plane of objective lens are directly projected on the detectors. Diffraction patterns contain useful crystallographic information associated with crystal orientation, space group symmetries in the crystal and lattice parameters.

In the present thesis, TEM was carried out in field-emission gun scanning transmission electron microscope FEI TalosTM F200 on thin lamella lift-out from the deformed micropillars to observe the dislocations interactions, identify the twin variants, and confirm the lack of precipitates. The observation of dislocations was

2.4 Micromachining using a focused ion beam (FIB)

carried in the two-beam condition based on the dislocation extinction condition in the BF imaging model by titling the sample stage in the TEM. The dislocations are not visible when the reflected beam ($\vec{g}$) is perpendicular to the Burgers vector ($\vec{b}$), $\vec{g} \cdot \vec{b} = 0$, and can be observed when $\vec{g} \cdot \vec{b} \neq 0$. The reflected beam was selected based on the diffraction pattern. The diffraction model was conducted to index the twinning variant after the micropillar compression deformation.

2.4 Micromachining using a focused ion beam (FIB)

A focused ion beam (FIB) instrument is generally installed in a SEM in the combined Dual-beam FIB-SEM systems. In the Dual-beam system, the electron and ion beams intersect at a 52° angle at a coincident point near the sample surface, as depicted in Figure 2.3. Commercially, the FIB imaging is acquired by scanning the sample surface with a focused beam of ions, such as Ga^+ . The Ga^+ ions are generated by a liquid metal ion source, which is a small Ga reservoir connected to a tungsten needle. Upon heating the reservoir, Ga flows to the tip of the needle, forming a small point source. A strong electric field is applied to the needle tip, and then extracts ions from this source. FIBs typically operate with an accelerating voltage between 1 and 50 keV. By controlling the strength of the electrostatic lenses and adjusting the effective aperture sizes, the probe current density (and therefore beam diameter) may be altered from tens of pA to several nA corresponding to a beam diameter of ~ 5 nm to ~ 0.5 μm [99].

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Figure 2.3 Schematic of the configuration of the dual beam FIB/SEM apparatus. The sample is tilted to 52° perpendicular to the ion beam.

The FIB systems can be used for imaging (operating at low beam currents), or for site specific milling and metal deposition and patterning at high beam currents [100]. During the FIB operation, Ga^+ ions are implanted in the sample and a small numbers of materials are sputtered including neutral atoms or sputtered ions, as well as emitted secondary electrons. The FIB imaging is acquired by collecting sputtered ions and the secondary electrons from the fine raster scanning on the sample surface. Modern FIB systems can achieve 5 nm imaging resolution [101]. At high ion current beams, large amounts of material can be removed from the sample surface by sputtering, and specimens with an arbitrary shape can be milled with precisions of the order of submicrometers or even, tens of nanometers. Additionally, FIB enables the localized maskless deposition of both metal and insulator materials, commercially platinum (Pt) and tungsten (W), to protect the selected area from the further implantation of the ions.

In this work, a Helios NanoLabTM DualBeamTM 600i FIB FEG-SEM microscope, as shown in Figure 2.4, was used to carry out the site-specific material milling process.

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Figure 2.4 FEI Helios NanoLabTM 600i dual-beam FIB-SEM microscope utilized in the present work consisting of: (1) Electron beam gun; (2) Gallium ion beam; (3) Metal deposition model; (4) EasyliftTM needle; (5) EBSD detector and (6) Chamber.

2.4.1 Micropillar fabrication

Micropillars were machined in the middle of individual grain of interest to avoid the grain boundary effect on the deformation process. A square cross-section shape was selected for the micropillars to facilitate the observation and analysis of the slip traces on the lateral surfaces after deformation. Micropillars with varying dimensions from $3 \times 3 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$ were fabricated to investigate the size effect on the mechanical deformation behavior. The aspect ratio height/lateral dimension was in the range 2:1 to 3:1 in all cases to avoid buckling for higher aspect ratios, or non-uniform stresses along the length for lower aspect ratios [102,103]. The stage with the sample in the microscope was firstly tilted to 52° to set the surface of interest perpendicular to the ion beam.

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Figure 2.5 SEM micrographs illustrating the micropillar milling procedure using the FIB.

The whole milling process can be divided into the following steps, as illustrated in the SEM micrographs in Figure 2.5. First, the position of interest away from the grain boundary was selected manually using the electron beam with the sample stage tilted at 52° . Second, rough milling with a high current beam of 9.3 nA was implemented to fast remove the material around the micropillar (Figure 2.5a). Third, the micropillar was milled using a current of 2.5 nA up to the final dimensions (Figure 2.5b). Fourth, a current of 0.79 nA was used to clean the rough lateral surface of the micropillars (depicted in Figure 2.5c). In this stage, the dimensions of the base of the micropillar were slightly larger than those at the top, leading to a taper angle of 1° to 2° . Fifth, the sample was tilted to 53.5° and the small current of 40 pA was employed to remove the taper of the micropillars and avoid the Ga^+ ions damage on the lateral surfaces of the micropillars. Finally, the sample was rotated 90° to remove the taper in each lateral surface, repeating the fourth and fifth steps. Afterwards, the micropillars

2.4 Micromachining using a focused ion beam (FIB)

with taper below 1° and aspect ratio in the range 2:1 to 3:1 were produced, as shown in Figure 2.5d. Accurate measurement of the height and the lateral dimensions was carried out with the sample tilted 45° and 0° , respectively from SEM images prior to deformation.

2.4.2 TEM lamella fabrication

After the micropillar compression tests, the deformed micropillars were carefully observed in the SEM to investigate the slip traces on the lateral surfaces. Then, a thin TEM lamella was extracted from the deformed micropillar to explore the dislocations and twin formation using TEM. The TEM lamella was prepared using the “lift-out” technique [99,104] with the FIB, so they can be extracted from the regions of interest. Figure 2.6 illustrates the typical procedure of the “lift-out” technique. The TEM lamella is prepared as follows:

- (i) The deformed micropillar of interest is selected, (Figure 2.6a).
- (ii) Pt was FIB-deposited on the lateral surface of the deformed micropillars under the ion beam to protect the lateral surface from the Ga^+ ion damage, as shown in Figure 2.6b).
- (iii) Another layer of Pt was deposited on the top surface of the deformed micropillars to avoid Ga^+ ion impinging the top surface, as shown in Figure 2.6c. The deposition process was initially carried out under the electron beam without tilting the sample, and then followed under the Ga^+ ion beam with the sample tilted 52° . The final thickness of the Pt layer was around $2\text{ }\mu\text{m}$.
- (iv) Afterwards, the rough cross-section milling of the trenches was performed on the either side of the Pt layer with the current of 9.3 nA to remove the surrounding material, leaving a thin wall of $\sim 2\text{ }\mu\text{m}$ thickness, as shown in Figure 2.6d.

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Figure 2.6 SEM micrographs illustrating the lift-out procedure to extract TEM lamella using the FIB.

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(v) A smaller beam current of 2.5 nA was employed to further thin the lamella to the thickness of approximately 1 μm . And the small current was used to reduce the Ga^+ ion damage to the surface of this membrane.

(vi) Then, the left and right sides of the membrane were cut away using the Ga^+ ion current of 2.5 nA, so that the membrane remained connected to the bulk substrate at the bottom, as shown in Figure 2.6e.

(vii) The thin lamella was transferred to a Cu grid, using a tungsten needle, which was attached to a micromanipulator. The tungsten needle was inserted and attached the left upper corner of the thin lamella, and glued by ion beam assisted Pt deposition. Then, the base of the lamella was cut away from the substrate using the Ga^+ ion current of 2.5 nA. The thin lamella was completely detached from the bulk substrate, as shown in Figure 2.6f.

(viii) Afterwards, the needle together with the thin lamella were lifted out and mounted on the Cu grid, using the Pt deposition, as shown in Figure 2.6g.

(ix) The final milling process was performed using a series of ion beam currents from 0.43 nA to 80 pA or 40 pA to ensure that the thickness was < 100 nm. The voltage and current were reduced to 5 keV and 15 pA to polish the thin lamella, ensuring minimum ion beam damage, as shown in Figure 2.6h. In order to eliminate the taper, the lamella was extra tilted by $1^\circ - 2^\circ$ with respect to the ion beam.

2.5 Micromechanical testing techniques

2.5.1 Instrumented nanoindentation

Nanoindentation system

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Nanoindentation systems have been extensively used in the last two decades to probe the mechanical behaviour of materials at small length scales [105–107]. During nanoindentation, a hard indenter is pressed against a flat surface of the sample. Different types of indenters with different geometries (such as Berkovich, Vickers, cube corner, conical or spherical) are widely employed to probe various mechanical properties, including hardness and elastic modulus [108–110], hardening exponents [111–113], creep properties [114–119], deformation instability [120,121], residual stresses [122–124], grain boundary strength [125–127], strain rate sensitivity [128,129] as well as the influence of temperature on these properties [130–132]. Nowadays, owing to the development of new sensors and actuators, the systems used for nanoindentation testing are capable of measuring contact forces and displacements in the nN and nm range, respectively, and have a spatial resolution below 1 μm for the position in the plane perpendicular to the indentation axis.

The load-displacement curves obtained from the nanoindentation tests are used to determine the mechanical properties. The crucial point in the analysis of the hardness and modulus relies on the determination of the contact area A_c of the residual imprint at the maximum load, which is traditionally measured by optical methods. This methodology clearly imposes a lower limit on the length scale of the indentation. This limitation was overcome by the protocol proposed by Oliver & Pharr [133] to estimate the contact area directly from the load-displacement curve, extending the scope of indentation testing to the nano-scale. The typical load-displacement curve obtained during nanoindentation is depicted in Figure 2.7a and shows the elastic and plastic regions. The elastic displacement during loading is recovered upon unloading. The estimation of the contact area A_c is obtained from the stiffness S of the unloading portion of the curve, as shown in Figure 2.7a.

Based on the Oliver & Pharr method [133], the contact area A_c is calculated as a function of the contact depth h_c , according to:

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$$A_c = F(h_c) \quad (2-1)$$

where $F(h_c)$ is a function, which depends on the geometry of the indenter. The functional form of F has to be established experimentally prior to analysis. The contact depth h_c is associated with the total depth at maximum load h_{max} and the displacement of the surface at the perimeter of the contact is expressed as (Figure 2.7b):

$$h_c = h_{max} - h_s \quad (2-2)$$

h_{max} can be directly obtained from the experimental measurement. Based on the Sneddon method [134], h_s can be derived as a function of the maximum load P_{max} and of the contact stiffness S obtained from the unloading portion according to:

$$h_s = \epsilon \cdot \left(\frac{P_{max}}{S} \right) \quad (2-3)$$

where ϵ is a geometric constant dependent on the indenter. For the flat punch, $\epsilon = 1$ while $\epsilon=0.72$ for a conical indenter and $\epsilon = 0.75$ for a Berkovich indenter. From this information and eq. (2-1), the contact area A_c can be calculated, and the hardness H and the reduced modulus E_r are given by:

$$H = \frac{P_{max}}{A_c} \quad (2-4)$$

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A_c}} \quad (2-5)$$

From the reduced modulus E_r , it is straightforward to determinate the elastic modulus of the material tested according to:

$$E = \frac{(1-v^2)}{\frac{1-v_i^2}{E_i} - \frac{1}{E_r}} \quad (2-6)$$

where E and v stand for the elastic modulus and the Poisson's ratio of the tested material, while E_i and v_i stand for the elastic modulus and Poisson's ratio of the indenter.

Figure 2.7 A schematic representation of (a) load-displacement curve showing the parameters used in the analysis as well as a graphical interpretation of the contact depth. (b) Cross section of an indentation showing the various parameters used in the analysis. h_{max} is the indentation depth at maximum load, h_c the contact indentation depth, h_f the final indentation depth after complete unloading and h_s the displacement of the surface at the perimeter of the contact [133].

Micropillar compression

Micropillar compression tests were developed by Dimiduk and Uchic [135] and have become a promising technique for determining the mechanical properties of various materials in the micrometer and sub-micrometer range. A flat-end punch tip was implemented in a conventional nanoindenter and used to compress the micropillar manufactured by the FIB. Thus, these tests mimic the compression tests commonly

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performed on macroscopic samples, with modifications to facilitate the fabrication and manipulation of the small specimens [136,137]. The main advantage of this technique, as compared with conventional nanoindentation, is that the stress state during the test is mainly uniaxial, leading to an obvious conversion of the measured load-displacement data into the engineering stress-strain curves, while a complex multi-axial stress-state is generated during nanoindentation. Thus, micropillar compression tests can be easily used to investigate the stress-strain behavior and deformation mechanisms at the micro-scale under simple, and well-established loading conditions.

During the micropillar compression tests, an extra compliance on the measured displacement would be introduced due to the elastic deformation of the substrate, which also acts as the lower compression plate. This effect has to be taken into account to obtain accurate strain and elastic modulus values and this is normally achieved by an analytical method, proposed by Sneddon [134,138], to account for the substrate deflection. The additional compliance associated with the elastic deflection of the surface as the base of the micropillar was expressed by C_{Sneddon} and it is given by:

$$C_{\text{Sneddon}} = \frac{\sqrt{\pi}(1-\nu^2)}{2E_{\text{base}}\sqrt{A_p}} \quad (2-7)$$

where E_{base} is the elastic modulus of the substrate material, A_p the instantaneous cross-sectional area of the micropillar, and ν the Poisson's ratio of the base material. Then, the deformation of the micropillar, u_{pillar} , was estimated from the measured total displacement according to:

$$u_{\text{pillar}} = u_{\text{total}} - C_{\text{Sneddon}}P \quad (2-8)$$

where P is the measured load, and u_{total} is the displacement obtained directly by the machine.

The engineering compressive stress τ and strain ε were computed from the initial

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length L_0 and the initial cross-sectional area A_0 of the micropillar according to:

$$\tau = \frac{P}{A_0} \quad (2-9)$$

$$\varepsilon = \frac{u_{pillar}}{L_0} \quad (2-10)$$

The micropillar compression tests were used in this thesis to ascertain the influence of solute atoms on the CRSS for basal slip and twinning in Mg-Al alloys as a function of micropillar size and temperature and to analyze the dominant deformation mechanisms.

The microscale experiments carried out in this work are associated with certain potential issues which should be explained in more detail to provide a better understanding of the research. Firstly, the misalignment between the flat punch tip and the micropillar surface may lead to the localization of the deformation in one region of the micropillar surface at the beginning of the test. This stress concentration may lead to an underestimation of the yield point and the elastic modulus, changes in the strain-hardening response and deformation mode as well as to buckling [103,139,140]. Thus, several protocols were used to minimize the misalignment, including to ensure that surface of the sample was flat during polishing and to correct the misalignment in the tests carried out *in situ* within the SEM.

Another potential problem is related to the pillar size effects, which can modify the obtained stress-strain response and the dominant deformation mechanism during the micropillar compression tests. It has been demonstrated that the yield/flow strength tend to increase as micropillar size decreases in many materials [141–146]. This “smaller is stronger” behaviour is mainly ascribed to the development of dislocation starvation [147] and dislocation source exhaustion mechanisms [148] that are triggered by the small volume of the material testes and the presence of many free surfaces from which the dislocations can escape. In this thesis, this size effect was estimated through micropillar compression tests in micropillars with sizes in the range

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3 μm to 7 μm .

2.5.2 Micromechanical testing apparatus

Two different commercial micromechanical testing platforms were employed in this investigation for the nanoindentation tests and the micropillar compression tests. The *ex situ* tests were carried out in a Hysitron TI950 TriboIndenter system and the *in situ* tests in Hysitron PI87 PicoIndenter system within the SEM as shown in Figure 2.8a and Figure 2.8b. The nanoindentation tests in the bulk material were mainly performed in the *ex situ* Hysitron TI950 TriboIndenter at room temperature, while the micropillar compression tests were conducted using both the *ex situ* Hysitron TI950 TriboIndenter system and the *in situ* Hysitron PI87 PicoIndenter system within the SEM at room temperature and elevated temperature.

Ex situ system

The *ex situ* nanoindentation and micropillar compression experiments were performed in a commercial TriboIndenter® TI950 nanoindentation system from Hysitron, Inc. (Minneapolis, MN), as shown in Figure 2.8a. This system makes use of a vertical axial-loading system based on a three-plate piezoelectric force transducer and capacitance depth-sensing indenter head. This system is a stand-alone platform, originally load-controlled. The load is applied in the vertical direction, electrostatically, and the displacement is measured through a patented design of a three-plate capacitive transducer. The system consists of four major components, including a low-load transducer, a high-low transducer and an optical microscope, which are fixed to the z-axis stage and installed in a granite bridge, as well as a X-Y positioning sample stage mounted on the bottom base, as depicted in Figure 2.8a. The low-load transducer provides a maximum force of 12 mN with a force resolution < 1

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nN and displacement resolution smaller than 0.02 nm. The high-load transducer presents a maximum force of 1 N with a force resolution below 1 μ N and displacement resolution lower than 0.1 nm. The equipment is located in an acoustic and thermal enclosure in order to minimize vibrations, thermal drift and acoustic noise during testing.

Figure 2.8 (a) Components of the Hysitron TI950 TriboIndenter system and (b) Schematic of the Hysitron PI87 PicoIndenter system. (1) High load transducer, (2) Low load transducer, (3) Optical microscope, (4) X-Y positioning stage.

As for nano-mechanical tests at elevated temperature, a hot stage (Hysitron xSol) and a flat punch probe fitted to a special long insulating shaft were used, as shown in Figure 2.9. In this configuration, the sample was placed between two resistive heating elements in order to eliminate temperature gradients across the sample thickness. Dry air and argon were used to purge the testing area around the tip and sample surface at the same time to prevent oxidation. Once the sample reached expected temperature, the tip was placed at about 100 μ m from the pillar surface for 10-15 minutes, to ensure

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passive heating of the tip before the start of the test and minimize thermal drift.

Figure 2.9 Schematic view of the xSol High Temperature Stage.

In-situ system

In situ micropillar compression tests were carried out using a commercial Hysitron PI 87 PicoIndenter system Inc. (Minneapolis, MN), (Figure 2.8b) inside the Helios NanoLab™ DualBeam™ 600i microscope (FEI) at room temperature and inside the ZEISS SEM EVO MA15 at elevated temperature, respectively. The *in situ* nanoindentation system is a miniaturised test platform for *in situ* materials characterization.

This system is a depth-sensing mechanical test instrument designed with a vacuum compatible transducer and an electrically conductive probe to perform quantitative nanomechanical testing while simultaneously leveraging the advanced imaging techniques of modern scanning electron microscopes, as shown in Figure 2.10. In this system, a force is applied electrostatically and the displacement is measured capacitively. This low-current design provides low thermal drift and a high stability and sensitivity. The system is equipped with two transducer models, including a low load transducer and a high load transducer. The low-load transducer has a maximum force of 16 mN with a force resolution lower than 1 nN and a displacement resolution below 0.02 nm, while the high-load transducer could achieve a maximum force of 500

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mN with a force resolution $< 1 \mu\text{N}$ and displacement resolution below 0.1 nm. The specimen is mounted on a piezo-actuated stage with 5 degrees of freedom (X, Y, Z rotation and tilt), allowing the accurate positioning for imaging with the different detectors and proper alignment between the load head and the specimen. The advanced positioning capabilities of the system enable a flexibility observation by additional detectors (EBSD, EDS, WDS, etc.) before, during or after the mechanical test. Furthermore, this system is capable of conducting micromechanical tests at high temperature within the ultra-high vacuum by incorporating tip and sample heaters with independent thermocouple-controlled feedback loops up to 800 °C.

Figure 2.10 Schematic of the in situ Hysitron PI87 PicoIndenter system.

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CHAPTER 3

Computational atomic mobility in hcp Mg-Al-Zn ternary alloys

3.1 Introduction

Reliable thermodynamic and kinetic database are critical to predict the materials structure, to control the phase transformation, internal precipitation reaction, as well as to simulate microstructure evolution, which have been used to develop advanced materials. Regarding the ternary Mg-Al-Zn alloys, a sound thermodynamic description was provided via CALPHAD (CALculation of Phase Diagram) by Liang et al. [149], taking into account the experimental data together with the constitutional, thermodynamic and crystallographic literature information, that could precisely predict the phase diagrams and properties of different phases.

3.2 Diffusion coefficients and atomic mobility

However, experimental diffusion data are limited and there is not yet any available kinetic database for the hcp phase of Mg-Al-Zn ternary system due to the experimental difficulties associated with melting high purity Mg alloys because of its high vapor pressure as well as the anisotropy of the hcp structure which complicates the diffusion behavior, as compared with cubic structures. Hence, the main objective of this investigation is to establish a set of atomic mobility parameters that dictate the kinetic behavior of ternary Mg-Al-Zn alloys. To this end, the experimental diffusion data in the Mg-Al, Mg-Zn and Mg-Al-Zn systems have been critically reviewed, including the impurity diffusion coefficients of Al and Zn in different Mg-based alloy systems along with the interdiffusion coefficients. Based on the composition profiles from the literature, the diffusion coefficients have been re-extracted using the Hall method for impurity diffusion, and the Sauer-Freise and the Whittle-Green strategies for interdiffusion coefficients in binary and ternary systems, respectively. From this information, the atomic mobility for the hcp phase of the Mg-Al, Mg-Zn and Mg-Al-Zn systems is obtained by using the parrot module of the DICTRA software. The diffusion profiles and diffusion paths are simulated from the optimized mobility parameters to provide further insight into the diffusion phenomena in the Mg-Al-Zn system.

3.2 Diffusion coefficients and atomic mobility

3.2.1 Determination of the diffusion coefficients

In the traditional method, the optimization of the atomic mobility is based on the experimental data on the tracer diffusion coefficients and the interdiffusion coefficients using the DICTRA software [150]. Particularly, the interdiffusion coefficients have to be extracted from the composition profiles of diffusion couples

3.2 Diffusion coefficients and atomic mobility

before the optimization.

The interdiffusion coefficients in the binary and ternary systems are mainly extracted using the Sauer-Freise method [151] and Whittle-Green method [152] based on the experimentally measured composition profiles, respectively. These two methods are improved to find an accurate interdiffusion coefficient as a function of composition, thereby avoiding the calculation of the Matano plane location. Before that, the raw measured composition profiles are firstly analytically represented by the error function expansion (ERFEX) [153] as follow:

$$x(\xi) = \sum_i a_i \operatorname{erfc}[b_i \xi - c_i] \quad (3-1)$$

where x is the composition of Al expressed in at.%, ξ the Boltzmann transformation variable, $\xi = z/\sqrt{t}$, z the diffusion distance, t the diffusion time and a_i , b_i and c_i are a series of adjustable parameters to fit the experimental profile to the ERFEX function. The origin for z in the composition profile is the point at which the Al content begins to increase from 0. As stated previously [154,155], the ERFEX function provides a precise and robust representation of discrete experimental data obtained from the EPMA measurement, while eliminating the point-to-point composition fluctuations, yet allows more sound physical meaning by applying the error function. This analytical representation of the diffusion profiles provided by ERFEX approximation is critical to attain reliable interdiffusion and impurity diffusion coefficients.

The phenomenological description of multicomponent diffusion originally proposed by Onsager [156,157], has been utilized for theoretical as well as experimental diffusion studies in multicomponent alloys. According to the Onsager's formalism [156,157], an extension of Fick's law has been demonstrated by Kirkaldy [158] in an n -component system given as following, with being referred to the laboratory-fixed frame with the molar volume of species i being assumed to be constant.

3.2 Diffusion coefficients and atomic mobility

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{i,j}^n \frac{\partial x_j}{\partial z} = \frac{1}{2t} \int_{x_i^- \text{ or } x_i^+}^{x_i} (z - z_0) dx_i \quad (i = 1, 2 \dots n) \quad (3-2)$$

where $\tilde{J}_i$ stands for the interdiffusion flux, which is determined directly from the composition profile of the individual component [159,160]. z_0 is the Matano plane for the diffusion couple. x_i is the mole fraction of species i , then x_i^- and x_i^+ represent the mole fractions of i at the far left and far right end of the diffusion couple. t is the diffusion time, and $\tilde{D}_{i,j}^n$ is the interdiffusion coefficient with n as the dependent species.

In both Sauer-Freise method [151] and Whittle-Green method [152], a normalized concentration variable is introduced, as follow, to avoid the inaccuracy induced by the position of the Matano plane.

$$Y_i = \frac{x_i - x_i^-}{x_i^+ - x_i^-} \quad (3-3)$$

According to Fick's second law of diffusion, an equation for the binary interdiffusion coefficient $\tilde{D}_{i,i}^n$ using the Sauer-Freise method [151] can be derived as following:

$$\tilde{D}_{i,i}^n = \frac{1}{2t} \frac{dz}{dY_i} \left[(1 - Y_i) \int_{-\infty}^z Y_i dz + Y_i \int_z^{+\infty} (1 - Y_i) dz \right] \quad (3-4)$$

Similarly, the Fick's second law in the ternary system can be expressed, as below, based on the Whittle-Green method [152]:

$$\frac{1}{2t} \frac{dz}{dY_i} \left[(1 - Y_i) \int_{-\infty}^z Y_i dz + Y_i \int_z^{+\infty} (1 - Y_i) dz \right] = \tilde{D}_{ii}^n + \tilde{D}_{ij}^n \frac{x_j^+ - x_j^-}{x_i^+ - x_i^-} \frac{dY_j}{dY_i} \quad (3-5)$$

$$\frac{1}{2t} \frac{dz}{dY_j} \left[(1 - Y_j) \int_{-\infty}^z Y_j dz + Y_j \int_z^{+\infty} (1 - Y_j) dz \right] = \tilde{D}_{jj}^n + \tilde{D}_{ji}^n \frac{x_i^+ - x_i^-}{x_j^+ - x_j^-} \frac{dY_i}{dY_j} \quad (3-6)$$

where $\tilde{D}_{ii}^n$ and $\tilde{D}_{jj}^n$ are the main interdiffusion coefficients, $\tilde{D}_{ij}^n$ and $\tilde{D}_{ji}^n$ the cross interdiffusion coefficients. Note that the determination of the four interdiffusion coefficients in the ternary system needs four equations to get a unique solution. Thus, the single interdiffusion coefficient at the intersection point where two diffusion paths

3.2 Diffusion coefficients and atomic mobility

cross could be obtained. Therefore, a large number of diffusion couples are required in order to derive the relationship between the interdiffusion coefficients and composition in the ternary system.

In addition, if the diffusion couple exhibits a maxima and/or minima in the composition profile, which is termed “Darken-type” diffusion couples [161], the extra interdiffusion coefficients can be determined. In the case of “Darken-type” diffusion couple, one of the main and one of the cross-interdiffusion coefficients at the extreme position can be obtained from the two composition profiles for the alloy species from the single diffusion couple. For instance, if there is a relative maximum or minimum for the species 1, but not for the other species 2, the concentration gradient of the species 1 is zero, namely $\frac{dx_1}{dz} = 0$, and the Eq. (3-6) can be simplified to:

$$\tilde{D}_{22}^n = \frac{1}{2t} \frac{dz}{dY_2} \left[(1 - Y_2) \int_{-\infty}^z Y_2 dz + Y_2 \int_z^{+\infty} (1 - Y_2) dz \right] \quad (3-7)$$

$$\tilde{D}_{12}^n = \frac{x_1^+ - x_1^-}{x_2^+ - x_2^-} \frac{dz}{dY_2} \cdot \frac{1}{2t} \left[(1 - Y_1) \int_{-\infty}^z Y_2 dz + Y_1 \int_z^{+\infty} (1 - Y_1) dz \right] \quad (3-8)$$

From this equation, $\tilde{D}_{22}^n$ and $\tilde{D}_{12}^n$ can be calculated from the single couple at the composition of the extrema in the profile of species 1. Similarly, $\tilde{D}_{11}^n$ and $\tilde{D}_{21}^n$ can be determined at the section where $\frac{dx_2}{dz} = 0$ if the species 2 also exhibits a maximum in the composition profiles.

If the concentration gradient of one species at the end of the couple approaches zero, meanwhile that of the other species is not equal to zero, ($\frac{dx_1}{dz} = 0$, while $\frac{dx_2}{dz} \neq 0$), in that case, the composition of species 1 will go up to the terminal composition (namely, $x_1 \approx x_1^+$ or x_1^-), and the Y_1 or $1 - Y_1$ will also be zero. Hence, only one main interdiffusion coefficient $\tilde{D}_{22}^n$ can be obtained by the single diffusion couple using equation (3-7), while the main-interdiffusion coefficient $\tilde{D}_{11}^n$ can be determined by the composition profile of species 1 at the end of the diffusion couple of species 2.

3.2 Diffusion coefficients and atomic mobility

3.2.2 Atomic mobility modeling

Andersson and Ågren [162] indicated that the most efficient way to establish a kinetic database for the diffusion is to use the atomic mobilities instead of the diffusion coefficients since the number of the diffusion coefficients in a system is much larger than that of the atomic mobilities. Therefore, the atomic mobilities are stored in the kinetic database and optimized to fit experimental diffusion data using the DICTRA software [150].

According to the absolute reaction rate theory, Andersson and Ågren [162] suggested a formalism for the atomic mobility M_i , expressed as a function of the absolute temperature T as below:

$$M_i = M_i^0 \exp\left(\frac{-Q_i}{RT}\right) \frac{1}{RT} \quad (3-9)$$

where M_i^0 represents the frequency factor with i standing for the species, and Q_i the activation energy. R and T are the gas constant and the absolute temperature, respectively. Both M_i^0 and Q_i depend on the composition and temperature. Jönsson [163] indicated that the logarithm of the frequency factor ($\ln(M_i^0)$) rather than M_i^0 varies linearly with the composition according to the empirical relation between the frequency factor and the composition found by Kučera and Million [164]. Thus, the diffusion mobility could be written as following:

$$M_i = \exp\left(\frac{RT \ln(M_i^0)}{RT}\right) \exp\left(\frac{-Q_i}{RT}\right) \frac{1}{RT} \quad (3-10)$$

Following the phenomenological approach, $RT \ln M_i^0$ and Q_i are assumed to be represented with a linear combination of the end-point values and a Redlich-Kister expansion [163,165], i.e.

3.2 Diffusion coefficients and atomic mobility

$$\Phi_i = \sum_p x_p \Phi_i^p + \sum_p \sum_{q>p} x_p x_q [\sum_{r=0,1,2,\dots}^r \Phi_i^{p,q} (x_p - x_q)^r] + \sum_p \sum_{p>q} \sum_{t>q} x_p x_q x_t [\sum_s v_{pqt}^s {}^s\Phi_i^{p,q,t}], (s = p, q, t) \quad (3-11)$$

where Φ_i stands for $RT \ln M_i^0$ or $-Q_i$. Φ_i^p is the value of Φ_i for i in species p . $\Phi_i^{p,q}$ and ${}^s\Phi_i^{p,q,t}$ represent the binary and ternary interaction parameters, respectively. v_{pqt}^s is introduced for the ternary system, given by $v_{pqt}^s = x_s + (1 - x_p - x_q - x_t)/3$. For a binary system, only the first two terms of the right-hand side of Eq. (3-11) have to be considered.

There are three types of diffusion coefficients based on the experimental conditions and the frame of reference:

1) tracer diffusion coefficient D_i^* (including the self-diffusion coefficient and impurity diffusion coefficient) determined from the diffusion studies using the radioactive isotopes in the lattice-fixed frame of reference and the secondary ion mass spectrometry (SIMS)-based thin-film technique [76];

2) intrinsic diffusion coefficient D_i measured by the implement of inert markers in the lattice-fixed frame of reference;

3) interdiffusion coefficient or chemical diffusion coefficient $\tilde{D}$ extracted from the composition profile of diffusion couple in the number-fixed frame of reference.

The tracer diffusion coefficient is directly correlated with the atomic mobility by the Einstein relation, i.e.

$$D_i^* = RTM_i \quad (3-12)$$

The intrinsic diffusion coefficient is determined by the atomic mobility and thermodynamic factors according to:

$$D_i = x_i M_i \frac{\partial \mu_i}{\partial x_i} \quad (3-13)$$

where μ_i is the chemical potential derived from the corresponding thermodynamic

3.3 Evaluation of experimental diffusivities

description.

The interdiffusion coefficient is calculated based on introducing an accurate thermodynamic description of the alloying system as following:

$$\tilde{D}_{pq}^n = \sum_i (\delta_{ip} - x_p) x_i M_i \left(\frac{\partial \mu_i}{\partial x_p} - \frac{\partial \mu_i}{\partial x_n} \right) \quad (3-14)$$

where δ_{ip} is the Kronecker delta ($\delta_{ip} = 1$ when $i = p$, otherwise $\delta_{ip} = 0$) and the index n stands for the dependent species. In this work, the parameters were obtained by fitting the experimental diffusion coefficients available in the literatures using an optimization algorithm.

The composition, varying with the diffusion time in the diffusion region of the diffusion couple, can be expressed as below:

$$\frac{1}{V_m} \frac{\partial x_i}{\partial t} + \nabla \cdot \tilde{j}_i = 0 \quad (3-15)$$

where V_m is the molar volume which is generally treated as constant, since the change of the molar volume during the diffusion process is negligible. $\tilde{j}_i$ is the interdiffusion flux of species i . The composition profiles could be expressed by solving numerically the eq. (3-15) with different initial conditions and boundary conditions.

3.3 Evaluation of experimental diffusivities

3.3.1 Impurity diffusion coefficients

The experimental impurity diffusion coefficient of Al into polycrystalline hcp-Mg has been determined by different researchers. Brennan [68,69] measured the Al impurity diffusion in polycrystalline hcp-Mg via the depth profiling with the secondary ion mass spectrometry method (SIMS) in the temperature range 573 K-673

3.3 Evaluation of experimental diffusivities

K. The thin film method and thin film solution of the diffusion equation were used to determine the diffusion coefficients. However, some artificial overestimation of the diffusion coefficients was introduced during the measurement process due to the surface roughness that resulted from the sputtering, especially at small grain sizes. And these data were considered to be unreliable as detailed in their research. Afterwards, in order to improve the experimental results, the solid-to-solid diffusion couples were implemented in polycrystalline hcp-Mg to measure Al impurity diffusion coefficients at 573 K, 623 K and 673 K by Brennan [67]. The impurity diffusion coefficients were determined according to the Boltzmann-Matano method [166] based on the composition profiles measured by the electron probe micro analysis (EPMA). However, the solubility of Al in hcp-Mg was so small at 573 K that the accuracy of these measurements was poor, and the experimental values at 573 K were not used in the current work. Kammerer et.al [65,66] studied the impurity diffusion behavior of Al and Zn in Mg using solid-to-solid diffusion couples in polycrystalline hcp-Mg in the temperature range from 623 K-723 K. The impurity diffusion coefficients were also calculated in the present work from the composition profiles using the Hall method [167], and they were used in our optimization.

Regarding the impurity diffusion of Zn in hcp-Mg, there are four main experimental studies. The radioactive ^{65}Zn isotope was diffused into polycrystalline hcp-Mg in the temperature range 498 K-848 K by Lal [74] and Čermák [70]. The composition depth profile was measured via the serial sectioning and residual activity methods. Additionally, the ^{65}Zn tracer diffusion series of experiments completed by Čermák [70] also reported the Zn impurity diffusion coefficients in three Mg- x Al solid solutions at temperatures between 648 K and 848 K. All the experimental impurity diffusion coefficients were used in the present optimization. Kammerer et al. [65,66] analyzed the diffusion couples between polycrystalline Mg and Mg-6.at% Zn alloy in the temperature range 623 K-723 K. And the impurity diffusion coefficient was calculated using the Hall method [167] in the present work from the experimental

3.3 Evaluation of experimental diffusivities

composition profiles, and was used in the optimization. The calculated Al and Zn impurity diffusion coefficients in the present work are depicted in Table 3.1.

Table 3.1 Al and Zn impurity diffusion coefficients calculated in this work using the Hall method from the experimental data [66]

Temperature (K)	D_{Al}^{Mg} (m^2/s)	D_{Zn}^{Mg} (m^2/s)
623 K	$1.81 \cdot 10^{-16}$	$3.31 \cdot 10^{-15}$
673 K	$0.92 \cdot 10^{-15}$	$2.21 \cdot 10^{-14}$
723 K	$5.12 \cdot 10^{-15}$	$5.79 \cdot 10^{-14}$
D_0 (m^2/s)	$1.38 \cdot 10^{-4}$	$8.68 \cdot 10^{-4}$
Q (kJ/mol)	143.02	138.74

3.3.2 Interdiffusion coefficients

There are few measurements for the interdiffusion coefficients in the hcp Mg-Al and Mg-Zn binary systems due to the limited solubility of Al and Zn in hcp-Mg. The composition dependence of the interdiffusion coefficients in Mg-Al polycrystalline were determined using the diffusion couples by Kulkarni [77] in the temperature range 653 K-693 K. And then, Kammerer et al. [65,66] investigated the interdiffusion coefficients in hcp Mg-Al and Mg-Zn alloys combining the diffusion-couple method in the temperature range 623 K-723 K. The interdiffusion coefficients were determined via the Sauer-Freise method [151] in the present work based on the experimental composition profiles measured by Kammerer et al. [65,66], and were utilized in the present optimization process.

Regarding the interdiffusion coefficients in hcp Mg-Al-Zn ternary system, the only experimental study was carried out by Kammerer et al. [79] in the temperature

range 673 K-723 K, by employing different solid-to-solid diffusion couples, (I: Mg-9 at.% Al/Mg-3 at.% Zn, II: Mg-3 at.% Al/Mg-1 at.% Zn, III: Mg/Mg-3 at.% Al-0.5 at.% Zn and IV: Mg/Mg-1 at.% Al-1 at.% Zn). The interdiffusion coefficients were determined in the present work based on these experimental composition profiles. Only two sets of interdiffusion coefficients were obtained at the intersection compositions of couple II and couple III together with couple II and couple IV at 723 K, as well as one set of couple II and couple III at 673 K. Besides, the main-interdiffusion coefficients $\tilde{D}_{Zn,Zn}^{Mg}$ were determined based on the couple I, II and III at both temperatures at the terminal ends of the composition profiles where the relative maxima and minima were found, expressed as “Darken-type” couple. Except for this, the impurity diffusion coefficients of Al in the Mg-Zn solid solution and Zn in the Mg-Al solid solution have also been confirmed from the composition profiles. All of these data were utilized in the assessment procedure to obtain a set of self-consistent parameters that reproduces the experimental results.

3.4 Atomic mobility assessment

A sound thermodynamic description of the Mg-Al-Zn ternary system was well developed by Liang et al. [149]. The thermodynamic parameters represented accurately the experimental phase diagram and thermodynamic properties. Therefore, these thermodynamic parameters have been directly adopted in the present work. The atomic mobility parameters were assessed on the basis of the available experimental data selected in the present work via Parrot module of the DICTRA software package, and the optimized parameters are listed in Table 3.2.

3.4 Atomic mobility assessment

Table 3.2 Optimized atomic mobility parameters obtained in this work.

Mobility	Parameter (J/mol)	Reference
Mobility of Mg		
Φ_{Mg}^{hcp-Mg}	-125077 - 88.17 * T	[80]
Φ_{Mg}^{hcp-Al}	-941760 + 63.18 * T	[80]
Φ_{Mg}^{hcp-Zn}	-91760 - 93.60 * T	This work
Mobility of Al		
Φ_{Al}^{hcp-Al}	-73360 – 95.08 * T	[168]
Φ_{Al}^{hcp-Zn}	-86960 - 93.60 * T	This work
Φ_{Al}^{hcp-Mg}	-143015 -73.88 * T	This work
${}^0\Phi_{Al}^{Al,Mg}$	581278 +114.95 * T	This work
${}^1\Phi_{Al}^{Al,Mg}$	820002 - 238.59 * T	This work
${}^0\Phi_{Al}^{Zn,Mg}$	-3918294 + 6114.65*T	This work
Mobility of Zn		
Φ_{Zn}^{hcp-Zn}	-91760 - 93.60 * T	[168]
Φ_{Zn}^{hcp-Al}	-91760 - 93.60 * T	[168]
Φ_{Zn}^{hcp-Mg}	-138743 - 58.61*T	This work
${}^0\Phi_{Zn}^{Zn,Mg}$	5183886 + 866.63 * T	This work
${}^1\Phi_{Zn}^{Zn,Mg}$	-6050970 + 324.68 * T	This work
${}^0\Phi_{Zn}^{Al,Mg}$	969245 + 369.11 * T	This work

${}^1\Phi_{Zn}^{Al,Mg}$	$1616532 - 241.02 * T$	This work
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3.4.1 Mg-Al binary system

Regarding the atomic mobility parameters for hcp Mg-Al binary system, Bryan et al. [80] performed a complete study of the atomic mobility in hcp Mg-Al alloys based on the critical revision of the available experimental data. However, their mobility parameters could not reproduce the experimental results very well, especially the experimental composition profiles measured by Kammerer et al. [65,66]. Hence, the mobility parameters were re-assessed in the present work on the basis of the interdiffusion coefficients and impurity diffusion coefficients calculated by our own code and the raw EPMA experimental composition profiles in order to improve the accuracy of the results.

The mobility parameter corresponding to the Al self-diffusion in hcp-Mg was evaluated by Bryan et al. [80] and satisfied the majority of the experimental diffusion data. And thus, it has been employed directly in the present work. Regarding the end-member for the Mg impurity diffusion in hcp Al (Φ_{Mg}^{hcp-Al}), it cannot be determined from the experimental data, because there is no stable hcp structure for Al. Thus, it was directly taken from the work of Bryan et al. [80]. The end-member parameter Φ_{Al}^{hcp-Mg} was optimized from the experimental data of the impurity diffusion coefficient [65–69], including results calculated in the present work from the composition profiles [66], which were firstly smoothed by the ERFEX method. And these data were given a higher weight during the optimization procedure due to their accuracy. The binary interaction parameters, ${}^0\Phi_{Al}^{Al,Mg}$ and ${}^1\Phi_{Al}^{Al,Mg}$ were assessed from the experimental interdiffusion coefficients [66,77] and the raw composition profiles measured by [66].

3.4 Atomic mobility assessment

The predictions of the impurity diffusion of Al in hcp-Mg obtained from the optimized atomic mobility parameters are plotted in Figure 3.1, together with the corresponding experimental data. They can be expressed as an Arrhenius-type equation, which depends on the frequency factor D_0 and the activation energy Q , which were given by $1.38 \times 10^{-4} \text{ m}^2/\text{s}$ and 143.02 kJ/mol , respectively. The predictions obtained from the optimized set of mobility parameters are in good agreement with the experimental data.

Figure 3.1 Variation of the Al impurity diffusion coefficient in pure Mg as function of the inverse of the absolute temperature. The solid line stands for the predictions with the optimized parameters, compared with the experimental data [65–69] as well as the values obtained in the present work.

The interdiffusion coefficients of the hcp Mg-Al obtained from the optimized mobility parameters are plotted in Figure 3.2 as a function of the Al content together with the experimental values from [66,77]. They are in good agreement at high temperature, but the calculated values overestimate the experimental results at 623 K because the experimental values of the interdiffusion coefficient remain practically constant with the Al content. This experimental result contradicts the empirical theory which establishes that the diffusion coefficients should increase if the addition of

alloying elements decreases the alloy melting point. Thus, the experimental data at 623 K are not very reliable and they were given a lower weight during the optimization process.

Figure 3.2 Interdiffusion coefficients of the hcp Mg-Al diffusion couples as a function of the Al content at 623 K, 673 K and 723 K. The solid lines stand for the predictions with the optimized parameters, compared with the experimental data [66,77] as well as the values obtained in the present work.

3.4.2 Mg-Zn binary system

In the Mg-Zn binary system, the parameter of impurity diffusion of Zn in hcp-Mg Φ_{Zn}^{hcp-Mg} , was directly optimized from the experimental data [65,66,70,74]. Among them, the impurity diffusion coefficients of Zn in hcp-Mg re-calculated in this work from the raw composition profiles [66] played a significant role in the optimization process. Due to the lack of experimental information about impurity diffusion of Mg in hcp-Zn, the end-member Φ_{Mg}^{hcp-Zn} was assumed to be equivalent to the self-diffusion coefficient of Zn. The binary interaction parameters ${}^0\Phi_{Zn}^{Zn,Mg}$ and ${}^1\Phi_{Zn}^{Zn,Mg}$

3.4 Atomic mobility assessment

were assessed according to the experimental interdiffusion coefficients and the composition profiles from [66].

Figure 3.3 Variation of the Zn impurity diffusion coefficient in pure Mg as function of the inverse of the absolute temperature. The solid line stands for the predictions with the optimized parameters, compared with the experimental data [65,66,70,74] as well as the values obtained in the present work.

The predictions from the optimized mobility parameters of the impurity diffusion of Zn in hcp-Mg with the temperature is compared with the experimental data from the literature [65,66,70,74], as depicted in Figure 3.3. They can be expressed as an Arrhenius-type equation, which depends on the frequency factor D_0 and the activation energy Q , which were given by $8.68 \times 10^{-4} \text{ m}^2/\text{s}$ and 138.74 kJ/mol in this work, respectively. The agreement between the calculation results and the critically reviewed experimental values is satisfactory. The calculated interdiffusion coefficients of the hcp Mg-Zn in the temperature range 623 K-723 K are presented with the experimentally measured data by [66] as a function of the Zn content, plotted in Figure 3.4. They are generally in good agreement although the experimental values show a little valley at 673 K, which means that the diffusion coefficients decrease as the Zn content increases. This is not reasonable, as indicated above, thus the weight of

this data was reduced in the optimization process.

Figure 3.4 Interdiffusion coefficients of the hcp Mg-Zn diffusion couples as a function of the Zn content at 623 K, 673 K and 723 K. The solid lines stand for the predictions with the optimized parameters, compared with the experimental data [66] as well as the values obtained in the present work.

3.4.3 Zn-Al binary system

There is obvious anisotropic diffusion behavior in hcp-Zn, owing to the hcp structure. Thus, the self-diffusion coefficients, parallel to c -axis and perpendicular to c -axis, are different. They have been well studied independently in the literature [84–86], and there no exists the experimental study related to the average self-diffusion coefficient of hcp-Zn. The end-member Φ_{Zn}^{hcp-Zn} was determined by Cui [168] based on the self-diffusion data for hcp-Zn [84–86], which was directly accepted in this work. In addition, there are not reliable experimental results for the self-diffusion of Al in hcp-Al, because there is no stable Al-hcp structure. The semiempirical self-diffusion relations have been employed to estimate the end-member Φ_{Al}^{hcp-Al} , following the theoretical estimations by Cui [168]. Regarding the impurity diffusion of Al in hcp-Zn, there is no available experimental data, because it is hard to melt high

3.4 Atomic mobility assessment

purity Zn due to its high vapor pressure. The end-member Φ_{Al}^{hcp-Zn} , was determined based on the experimental data of the impurity diffusion coefficients of Ga in hcp-Zn [169], assuming that Ga has the similar properties with Al from the diffusion viewpoint.

Moreover, the parameters parallel to the *c*-axis were selected in the present work as the average values in the cases where average values were not available. Since the present results were focused in the region with high Mg content, the parameters of the region with high Zn content have limited influence. And there is no available experimental study for hcp phase in Zn-Al solid solution due to the small solubility of Al in hcp-Zn. Thus, the interaction parameters for Zn-Al binary system are missing.

3.4.4 Mg-Al-Zn ternary system

The parameters $\Phi_{Zn}^{Al,Mg}$ and $\Phi_{Al}^{Zn,Mg}$ were assessed from the raw composition profiles and the impurity diffusion coefficients of Zn in Mg-Al alloys and Al in Mg-Zn alloys extracted in this work from the composition profiles. The ternary interaction parameters played a negligible role in the atomic mobility on account of the limited solubility of Al and Zn in hcp Mg alloy, and were assumed to be zero.

The predictions based on the optimized mobility parameters of the impurity diffusion coefficients of Al in Mg-Zn alloy and of Zn in Mg-Al are depicted as a solid line in Figure 3.5a and Figure 3.5b, respectively, together with the calculated values obtained from the original composition profiles as well as from the available experimental data in literature [65,70]. It is evident that there is a large deviation in the predictions of the Al impurity diffusion coefficients, especially at lower Zn composition, as shown in Figure 3.5a, which may be due to errors introduced during the calculation by the Hall method. The calculated Zn impurity diffusion coefficients in Mg-Al alloy are plotted as solid lines in Figure 3.5b and compared with the

3.4 Atomic mobility assessment

experimental data obtained from the diffusion couples [65,70]. The calculated values behave in better accord with the major of the experimental data, although the experimental values [70] lead to slightly higher coefficients than the calculated results.

Figure 3.5 The experimental impurity diffusion coefficients of (a) Al in hcp Mg-Zn alloy with the experimental values [65]; (b) Zn in hcp Mg-Al alloy with the experimental data [65,70] compared with the values obtained in the present work from the composition profiles. The solid lines stand for the predictions with the optimized parameters.

Table 3.3 Interdiffusion coefficients ($D \times 10^{-15} \text{m}^2/\text{s}$) at 673 K and 723 K extracted from the diffusion couple experiments of Kammerer [65].

Temp	Couple	Al.at%	Zn.at%	$\tilde{D}_{Al,Al}^{Mg}$	$\tilde{D}_{Al,Zn}^{Mg}$	$\tilde{D}_{Zn,Zn}^{Mg}$	$\tilde{D}_{Zn,Al}^{Mg}$
673 K	II-III	2.68	0.28	0.63	0.11	10.90	14.40
	II-IV	0.80	0.63	0.57	1.60	37.95	3.54
723 K	II-III	2.75	0.24	25.71	3.85	70.19	15.85

The interdiffusion coefficients at 673 K and 723 K at common intersection compositions were obtained based on the experimental composition profiles, and they are presented in Table 3.3 (Figure 3.6). It is evident that Zn diffuses much faster than

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Al, since the main-diffusion coefficient of Zn is one order of magnitude greater than that of Al. There appears a relative maxima in the profiles, where the concentration gradient of Al goes up to zero, while that of Zn does not. Based on “Darken-type” couple method, one main-interdiffusion coefficient can be determined at the relative maxima, and it is reported in Figure 3.4 (Figure 3.6).

Figure 3.6 The main-interdiffusion coefficients of Zn ($\bar{D}_{Zn,Zn}^{Mg}$) in the Mg-Al-Zn alloys (a) at 673 K and (b) at 723 K.

3.5 Diffusion simulation

Table 3.4 Main-interdiffusion coefficients of Zn ($D \times 10^{-14} \text{m}^2/\text{s}$) at relative maxima compared with the values obtained from the optimized mobility parameters.

Temp	Couple	Al.at%	Zn.at%	$\tilde{D}_{Zn,Zn}^{Mg}$	$\tilde{D}_{Zn,Zn}^{Mg}$
				experiment	optimized
673 K	I	9.06	0.10	3.52	3.58
		0.00	2.15	1.97	3.15
	II	0.02	0.90	1.79	1.62
		2.70	0.07	0.60	0.81
	III	2.68	0.31	0.95	0.88
		0.00	0.07	1.38	1.48
	IV	0.87	0.89	3.22	1.34
		0.00	0.25	5.24	1.48
723 K	I	9.10	0.12	13.48	28.18
		0.02	1.86	15.64	16.07
	II	2.77	0.03	6.31	5.25
		0.00	0.96	11.62	9.93
	III	2.79	0.30	5.26	5.84

3.5 Diffusion simulation

To validate the present assessed atomic mobility parameters, the composition profiles in the binary and ternary systems as well as the diffusion paths are predicted,

3.5 Diffusion simulation

on the basis of the optimized mobility parameters in Table 3.2, together with corresponding thermodynamic database.

3.5.1 Composition profiles of diffusion couples

The composition profiles for the Mg-Al binary system calculated from the optimized mobility parameters are compared in Figure 3.7 with the raw experimental data obtained from the diffusion couples from the literature [66]. The agreement is very good at 673 K and 723 K, but there are large differences at 623 K, which may be due to the discrepancy in the interdiffusion coefficients curves, as indicated in Section 3.4.1. Similarly, the comparison between the simulated and experimental composition profiles in Mg-Zn alloy are depicted in Figure 3.8 and behaves a better consistency. The present calculated results are in good accordance with the corresponding experimental data [66]. As it can be seen at 673 K, the interdiffusion coefficients witnesses an obvious downtrend on the side of Mg-Zn solid solution. This is not reasonable, as it was already indicated in Section 3.3.2.

Representative composition profiles calculated from the optimized parameters for the ternary couples are plotted in Figure 3.9, together with the experimental data. Figure 3.9a and Figure 3.9b show the calculated composition profiles of the diffusion couple I (Mg-9 at.%Al/Mg-3 at.%Zn annealed at 673 K for 8 hours) and of the diffusion couple II (Mg-3 at.%Al/Mg-1 at.%Zn annealed at 723 K for 5 hours), along with the raw EPMA experimental data [79]. Overall, the simulated composition profiles fit well with the experimental values in these cases. The calculated and experimental composition profiles for the diffusion couple IV (Mg/Mg-1 at.%Al-1 at.%Zn annealed at 673 K for 24 hours) are demonstrated in Figure 3.9c and there are large differences in the composition profiles of Zn. As shown in Table 3.4, the calculated main-interdiffusion coefficients for Zn of couple IV are about four times higher than

3.5 Diffusion simulation

those obtained from the experimental data of couple III. These differences in the interdiffusion coefficients with similar compositions are not reasonable and the experimental data for couple IV were not used in the optimization.

Figure 3.7 Composition profiles calculated from the optimized parameters and experimental values [66] of diffusion couples in Mg-Al alloys: (a) 623 K; (b) 673 K; (c) 723 K. The solid lines represent the predictions with the optimized parameters.

The comparison between the simulated and experimental composition profile of diffusion couple I annealed at 723 K is implied in Figure 3.9d, and discrepancies are observed at the terminal end of Al composition profile. The deviation results from the impurity diffusion coefficient of Al in Mg-Zn alloy that should be adjusted consistently with other experimental data. Nevertheless, these differences are

3.5 Diffusion simulation

acceptable taking into account the general agreement with the experimental data. It can be clearly seen from the Figure 3.9 that Zn diffuses faster than Al in the ternary system according to the longer diffusion distance of Zn in the solid solutions. The good agreement between the simulated composition profiles and the experimental results validate the assessed atomic mobility in the present work.

Figure 3.8 Composition profiles calculated from the optimized parameters and experimental values [66] of diffusion couples in Mg-Zn alloys: (a) 623 K; (b) 673 K; (c) 723 K. The solid lines represent the predictions with the optimized parameters.

Figure 3.9 Composition profiles calculated from the optimized parameters and experimental values [79] in hcp Mg-Al-Zn alloys: (a) Couple I annealed at 673 K for 8 h; (b) Couple IV annealed at 673 K for 24 h; (c) Couple II annealed at 723 K for 5 h; (d) Couple I annealed at 723 K for 4 h. The solid lines represent the predictions with the optimized parameters.

3.5.2 Diffusion paths

Figure 3.10a and Figure 3.10b depict the diffusion paths calculated from the optimized parameters for various ternary diffusion couples annealed at 673 K and 723 K respectively, which are compared with corresponding experimental data [79]. Note that the diffusion paths are expressed to be S-shaped curves. There is an empirical trend that the initial directions of the diffusion paths tend to be aligned with the line of

3.6 Conclusions

constant composition of the slower diffusion species in the diffusion zone. Meanwhile, the diffusion paths can distinguish the diffusion rates for different species, based on the difference in the greater degree of curvature and the shape of the diffusion paths. The majority of the calculated diffusion paths show good agreement with the corresponding experimental values, with the exception of couple I at both temperatures. The departure of several points from the calculated curves comes from the slight deviation in the composition profiles of diffusion couple I at the terminal end of the Zn profile at 673 K and that of the Al profile at 723 K. Regardless of this discrepancy, the optimized parameters provide acceptable predictions taking into account their ability to reproduce the overall diffusional behavior of the Mg-Al-Zn system.

Figure 3.10 Comparison between the calculated diffusion paths and the available experimental data [79] (a) at 673 K and (b) 723 K. The solid lines stand for the predictions with the optimized parameters.

3.6 Conclusions

The work carried out in this chapter investigated the diffusion behaviour of the

Mg-Al-Zn ternary system in the polycrystalline. And the atomic mobility was assessed based on the experimental data employing the CALPHAD method. It mainly revealed the diffusion behavior in the polycrystalline alloys, combining the contributions of the grain boundaries and grain orientation effect to the diffusion coefficients.

The experimental data related to the diffusion coefficients of the hcp Mg-Al-Zn alloys available in the literature has been critically reviewed. Based on the composition profiles from the literature, the diffusion coefficients at various temperatures have been re-extracted in this investigation using the Hall method for impurity diffusion, and the Sauer-Freise and the Whittle-Green strategies for interdiffusion coefficients in binary and ternary systems, respectively. In addition, the composition profiles with relative maxima have been analyzed by the “Darken-type” couple method. On basis of these data, the atomic mobility of Al, Zn and Mg in hcp Mg-Al-Zn ternary alloys has been assessed, via the Parrot Model of DICTRA software package in conjunction with the corresponding thermodynamic database. The optimized set of atomic mobility parameters could successfully predict the diffusion behavior for binary and ternary diffusion couples. Comprehensive comparisons between the simulated and the measured diffusion coefficients data show an excellent agreement not only for the composition profiles but also for the diffusion paths, hence further validating the assessed parameters. And it is observed that Zn diffuses faster than Al in the ternary system.

3.6 Conclusions

CHAPTER 4

Effect of solid solute on the anisotropic interdiffusion behavior

4.1 Introduction

The majority of the investigations on the diffusion behavior in Mg alloys was performed in polycrystalline Mg or Mg alloys, which included the contribution from all grains with different orientations. However, the interdiffusion behavior is expected to be anisotropic in hcp Mg, as stated in the Chapter 1. Therefore, a robust approach is required that could explore efficiently the anisotropic interdiffusion behavior to extract essential diffusion data as a function of the grain orientation. In this chapter, a high-throughput experimental approach is presented to determine the anisotropic

4.2 Experimental procedure

diffusion behavior of hcp crystals, for Mg-Al alloy. The approach combines polycrystalline diffusion couples with the information about the grain orientation along the diffusion path. The composition profiles are analyzed in the diffusion region across multiple grains. The anisotropic diffusion coefficients were obtained as a function of the alloy composition and grain orientation using the forward-simulation scheme for multi-grain diffusion. This information was used to obtain the interdiffusion coefficients in the orientation perpendicular $D_{\perp}$ and parallel $D_{\parallel}$ to the c axis as a function of Al solute content at 673 K and 723 K using a novel splitting technique.

4.2 Experimental procedure

The polycrystalline diffusion couple, Mg/Mg-9 at.%Al, was fabricated from high-purity Mg (99.99 wt.%) and Al (99.99 wt.%) as indicated in sections 2.1 and 2.2. Specimens were cut along the direction perpendicular to the contact plane from the diffusion couple. The local compositions throughout the interdiffusion regions were analyzed by electron probe microanalysis (EPMA) using Wavelength Dispersive Spectroscopy (WDS) with a voltage of 20 KV and a beam current of 50 nA in the JEOL Superprobe JXA-8900M. In particular, the composition profile was measured along lines parallel to the diffusion direction, which were perpendicular to the interface of the diffusion couples (Figure 4.1). The microstructure was characterized by the scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) in a high-resolution scanning electron microscope (Helios NanolabTM 600i FEI) equipped with an Oxford EBSD system. The EBSD measurements were conducted at the same locations where the diffusion profiles were measured using an accelerating voltage of 30 KV and a beam current of 2.7 nA with a step size of 1.5 μm . The EBSD maps provide the rotation angle θ , that specifies the misorientation

between the diffusion direction and the c axis of each grain (Figure 4.1). The diffusion direction (marked by a blue arrow) was vertical to the interface of the diffusion couple in the reference coordinate system denoted in Figure 4.1. Note that the rotation angle θ for each grain is directly obtained from the Euler angle provided by the EBSD measurements.

Figure 4.1 Schematic representation of the rotation angle θ between the diffusion direction (DD) and the c axis of each grain.

4.3 Diffusion data analysis

The anisotropic interdiffusion coefficient $\tilde{D}(x, \theta)$ within the interdiffusion region depends on both the grain orientation, indicated by the rotation angle (θ), and the Al content (x). The analysis of the local composition profiles within the interdiffusion region in the diffusion couples can be used to extract the anisotropic interdiffusion coefficient $\tilde{D}(x, \theta)$ for a large range of compositions and grain orientations. Afterwards, it was assumed that the experimental values of $\tilde{D}(x, \theta)$ could be expressed as a function of two interdiffusion coefficients $D_{\perp}$ and $D_{\parallel}$ along the basal plane and parallel to the c axis of the Mg hcp lattice, respectively (Figure 4.2).

4.3 Diffusion data analysis

Figure 4.2 Schematic representation of the anisotropic diffusion coefficients. The blue line stands for the diffusion direction, perpendicular to the interface indicated by the black dotted line, and the two components $D_{\perp}$ and $D_{\parallel}$ are represented by the green arrow line.

4.3.1 Extraction of interdiffusion coefficients

Eight specimens were sliced for analyzing the composition and characterizing the microstructure and grain orientation in this investigation, four of them were cut with great caution from the diffusion couples annealed at 673 K, and the other four were from 723 K. The microstructure and grain orientation information provided by EBSD measurement in the diffusion region of these eight specimens are shown in Figure 4.3, where the grain color stands for the rotation angle θ between the c axis of the grain and the diffusion direction. The composition profiles were measured by EPMA along the black lines (parallel to the diffusion direction) marked in each specimen, as depicted in Figure 4.3. The left end of the diffusion couples corresponds to the pure Mg side while the right end stands for the Mg-Al alloy. It can be observed clearly that the interdiffusion region generally contains multiple large grains, since it is hardly to obtain a diffusion couple that includes a single grain across the diffusion region because of the development of recrystallization during the high temperature annealing along the diffusion interface. These grains within the interdiffusion region are quite large (several hundreds of microns), and the measured composition profiles generally pass through multiple grains (Figure 4.3). It should be noted the grain size in the Mg-

4.3 Diffusion data analysis

rich region of the diffusion couple is sometimes quite small as $\sim 50 \mu\text{m}$ (particularly in the samples annealed at 723 K), and the composition profile generally passes through multiple grains which were not considered in this investigation.

Figure 4.3 Microstructure of the diffusion couples in the diffusion region. (a)-(d) Specimens annealed at 673 K. (e)-(h) Specimens annealed at 723 K. The color code stands for the grain orientation according to the inverse pole figure. The composition profile was measured along the black lines by EPMA.

The strategy to obtain the anisotropic diffusion coefficients from the composition profile is detailed below for the representative example in Figure 4.4a. In this case, the composition profile is obtained along the black line parallel to the diffusion direction across three grains, Grain 1, 2 and 3, with the rotation angle of 5° , 29° and 33° respectively, as shown in (Figure 4.4a). And the length of the composition profile to determine the interdiffusion coefficients is around 1 mm. The Al content along this line is given by the blue circles superposed to the microstructure in Figure 4.4b, which enlarges the square region in Figure 4.4a. The raw measured composition profiles are analytically represented by the error function expansion (ERFEX) [153] according to eq. (3-1) as described in Section 3.2.1 And a series of adjustable parameters, a_i , b_i and c_i , are obtained by fitting the experimental profile to the ERFEX function. The origin for distance z of the composition profile in Figure 4.4b is the point for which the Al

4.3 Diffusion data analysis

content begins to depart from 0.

Figure 4.4 (a) Microstructure in the diffusion zone where the color code indicates the grain orientation according to the inverse pole figure (IPF). (b) The experimental composition profile (blue circles) measured by EPMA along the black line in (a), combined with the analytical fit using the ERFEX error expansion function. (c) Extracted interdiffusion coefficients as a function of the Al content for each grain.

Since the diffusion profile usually passes multiple grains with diverse grain orientation, the interdiffusion coefficients along the composition profile also depend on the grain orientation. The interdiffusion coefficients in each grain, $\tilde{D}(x, \theta)$, were obtained using the forward-simulation scheme originally developed by Zhang and Zhao [170] for multi-phase diffusion. To do this, they were firstly determined using the traditional Boltzmann-Matano [166] method or the Sauer-Freise method [151]. $\tilde{D}(x, \theta)$ was assumed to be expressed by a quadratic function of the Al content (in

at. %) in each grain according to:

$$\text{Log}_{10} \tilde{D}(x, \theta) = p_i x^2 + q_i x + r_i \quad (4-1)$$

where p_i , q_i and r_i stand for the fitting parameters, which vary with the grain orientation. Then, the composition profile in each grain was simulated by solving Fick's second law of diffusion, based on the assumed diffusion coefficients given by eq. (4-2), which was transformed into an ordinary differential equation by applying the Boltzmann transformation,

$$-\frac{\xi}{2} \frac{dx}{d\xi} = \frac{d}{d\xi} \left(\tilde{D}(x, \theta) \frac{dx}{d\xi} \right) \quad (4-2)$$

Then, the fitting parameters in the eq. (4-2) were adjusted to fit the experimental composition profile for each grain in Figure 4.4b and the interdiffusion coefficient was obtained. Note that the continuity of the diffusion flux across grain boundaries was assumed because the grain boundary width is negligibly small compared to the typical diffusion distance ($\sim$ mm).

The interdiffusion coefficients for grains G1, G2 and G3 are plotted in Figure 4.4c as function of the Al content. As expected, the variation of the interdiffusion coefficients with the Al content was different in each grain because the differences in the grain orientation.

4.3.2 Determination of $D_{\perp}$ and $D_{\parallel}$

After the interdiffusion coefficients were obtained as a function of the grain orientation and composition, $\tilde{D}(x, \theta)$, the anisotropic interdiffusion coefficients $D_{\perp}$ and $D_{\parallel}$ were determined using the theoretical framework proposed by Shewmon [91], which assumed that:

4.3 Diffusion data analysis

$$\tilde{D}(x, \theta) = D_{\perp}(x)\sin^2(\theta) + D_{\parallel}(x)\cos^2(\theta) \quad (4-3)$$

where the $D_{\perp}(x)$ and $D_{\parallel}(x)$ could be expressed using an Arrhenius law, leading to:

$$D_{\perp}(x) = D_{\perp 0}(x)\exp\left(-\frac{Q_{\perp}(x)}{RT}\right) \quad (4-4)$$

$$D_{\parallel}(x) = D_{\parallel 0}(x)\exp\left(-\frac{Q_{\parallel}(x)}{RT}\right) \quad (4-5)$$

where $D_{\perp 0}(x)$ and $Q_{\perp}(x)$ are the frequency factor and diffusion activation energy within the basal plane, whilst $D_{\parallel 0}(x)$ and $Q_{\parallel}(x)$ stand for the corresponding values parallel to the c axis of the grain. In the present work, it was assumed that both the activation energy and the frequency factor have a linear dependence with the composition according to:

$$D_{\perp 0}(x) = a_{\perp}x + b_{\perp} \quad D_{\parallel 0}(x) = a_{\parallel}x + b_{\parallel} \quad (4-6)$$

$$Q_{\perp}(x) = c_{\perp}x + d_{\perp} \quad Q_{\parallel}(x) = c_{\parallel}x + d_{\parallel} \quad (4-7)$$

where $a_{\perp}$, $b_{\perp}$, $c_{\perp}$, and $d_{\perp}$ (and $a_{\parallel}$, $b_{\parallel}$, $c_{\parallel}$, and $d_{\parallel}$) are the fitting parameters. In case of more complex compositional dependency, a quadratic function could be assumed as well. They were obtained from the experimental values of $\tilde{D}(x, \theta)$ through eq. (4-3) using the least squares fitting and, then, $D_{\perp}$ and $D_{\parallel}$ can be determined.

4.3.3 Effect of grain boundary on interdiffusion coefficients

In practice, it is hard to obtain a diffusion couple that includes a single grain across the diffusion region because of the nucleation and growth of new grains along the diffusion interface during the high temperature annealing, as shown in Figure 4.5. As the diffusion rate of the Al atoms along the grain boundaries is known to be two orders magnitude faster than that in bulk Mg [171], it is important to eliminate any grain boundary contribution in the regions of the diffusion couple used to determine the diffusion coefficients.

4.3 Diffusion data analysis

The effect of grain boundaries on the composition profile is shown in Figure 4.5 for two typical cases found in the diffusion couples. In the first case (Figure 4.5a), the composition profile was measured along the red line S1 which crossed three grains denoted A, B, and C. The grain boundaries A/B and B/C were perpendicular to the composition line S1. In the other case (Figure 4.5b), a small grain F was found between the large grains E and G. The composition profile was measured along two lines, the black solid line S2a and blue dashed line S2b. Both lines were perpendicular to the grain boundary E/G, but the line S2a was located close to (around 40 μm away) the grain boundary E/F, which was parallel to the line S2a.

Figure 4.5 Microstructure of the diffusion couple near the diffusion interface of the two typical cases. The colour code indicates the grain orientation (according to the IPF). Grain boundaries are delineated by blue lines. (c) Interdiffusion coefficients extracted from the composition profiles along the lines S1 and S2a and S2b.

The interdiffusion coefficients extracted from the composition profiles along the three lines in Figure 4.5a and Figure 4.5b using the methodology indicated above are plotted as a function of the Al content in Figure 4.5c. Of course, the orientation of each grain was different and thus, the interdiffusion coefficients were different for each grain. There was not kink at the grain boundaries in the case of the lines S1 and S2b, because these lines were perpendicular to the grain boundaries and the grain boundary leakage (perpendicular to the diffusion direction) did not influence the

4.4 Results and discussion

measurements. Nevertheless, the interdiffusion coefficients increased by a factor of 7 along the line S2a in the region close the grain boundary E/F. Thus, only composition profiles far away ($> 100 \mu\text{m}$) of any lateral grain boundary in Figure 4.3 were used to determine the interdiffusion coefficients to avoid the effect of grain boundary leakage. It should be noted that they were mainly found in the Mg-Al part of the diffusion couple (Figure 4.3) because recrystallization occurred often during annealing in the soft Mg region of the diffusion couple, leading to the development of small grains.

4.4 Results and discussion

4.4.1 Influence of grain orientation on the interdiffusion coefficients

Composition profiles perpendicular to the diffusion interface were obtained along scan lines which did not have any grain boundary close to the scan line (such as the S1 scan line in Figure 4.5a) to avoid the effect of grain boundaries. The interdiffusion coefficients for grains with different orientations were extracted with the forward-simulation scheme described in Section 4.3, and the p_i , q_i and r_i coefficients that indicated the influence of the Al content on the interdiffusion coefficients for the rotation angle θ are given in Table 4.1. The interdiffusion coefficients $\tilde{D}(x, \theta)$ were assumed to be expressed by a quadratic function of the Al content (in at. %) in each grain using eq. (4-1).

4.4 Results and discussion

Table 4.1 Coefficients of eq. (4-1) to express the interdiffusion coefficients as a function of Al content for different rotation angles θ

Temp (K)	Rotation angle	p_i	q_i	r_i
673 K	5.8°	-362.8237	61.2367	-35.5152
	33°	-128.4483	32.9941	-34.7475
	44°	53.9833	-1.4807	-33.0104
	75°	34.7870	1.5273	-33.0756
723 K	5.3°	266.6762	-19.9245	-31.1241
	28°	450.7663	-33.9376	-31.1299
	53°	614.2203	-47.3864	-30.6317
	81°	320.2773	-41.5305	-29.7505

The influence of the grain orientation (described by θ) on the interdiffusion coefficients is shown in Figure 4.6. The results in Figure 4.6a summarize the interdiffusion coefficients from Mg-5 at.%Al to Mg-8.5 at.%Al at 673 K whereas those in Figure 4.6b cover the compositions from Mg-5.5 at.%Al to Mg-7.5 at.% Al at 723 K. These results show that the interdiffusion coefficients increase with the Al content as well as with θ , indicating that diffusion along the basal plane was faster than along the c axis. Similar trends were found for the Al and Zn impurity diffusion coefficients in Mg [93]. Nevertheless, a minimum in the diffusion coefficients is found for $\theta \sim 30^\circ$, as shown in Figure 4.6b, and this minimum is present for all the different Al contents. The minima are being further scrutinized by our ongoing experimental investigation and theoretical treatment.

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Figure 4.6 Influence of the rotation angle θ on the interdiffusion coefficients in Mg-Al alloys. (a) From Mg-5 at.% Al to Mg-8.5 at.% Al at 673 K. (b) From Mg-5.5 at.% Al to Mg-7.5 at.% Al at 723 K.

The two interdiffusion coefficients $D_{\perp}(x)$ and $D_{\parallel}(x)$ along the basal plane and the c axis were obtained from the interdiffusion coefficients following the splitting scheme described in Section 4.3.2 and they are plotted in Figure 4.7. Moreover, the parameters in eqs. (4-6) and (4-7) to obtain the interdiffusion coefficients as a function of the Al content and temperature are listed in Table 4.2. As expected, $D_{\perp}(x)$ and $D_{\parallel}(x)$ increase with the Al content and with temperature. Note that the interdiffusion along the basal plane is always faster than along the c axis for the same Al content and temperature, and that the differences decrease as the Al content increased.

Table 4.2 Parameters to derive the diffusion activation energy and frequency factor of the interdiffusion coefficients along the basal plane ($D_{\perp}(x)$) and the c axis ($D_{\parallel}(x)$) as defined by eqs. (4-6) and (4-7).

$D_{0\perp}$ (m ² /s)		$Q_{\perp}$ (J/mol)		$D_{0\parallel}$ (m ² /s)		$Q_{\parallel}$ (J/mol)	
$a_{\perp}$	$b_{\perp}$	$c_{\perp}$	$d_{\perp}$	$a_{\parallel}$	$b_{\parallel}$	$c_{\parallel}$	$d_{\parallel}$
$9.42 \cdot 10^{-3}$	$1.33 \cdot 10^{-4}$	$24.2 \cdot 10^3$	$1.42 \cdot 10^5$	$2.10 \cdot 10^{-2}$	$3.03 \cdot 10^{-4}$	$1.10 \cdot 10^4$	$1.49 \cdot 10^5$

Figure 4.7 $D_{\perp}(x)$ and $D_{\parallel}(x)$ interdiffusion coefficients as a function of the Al content at 673 K and 723 K.

The accuracy of the interdiffusion coefficients was confirmed by the comparison between the experimental and the calculated interdiffusion coefficients in the present work, shown in Figure 4.8. The dashed lines refer to the generally accepted deviation range of a factor between 0.5 and 2. A good accordance between the calculated values and experimental data is achieved in this investigation. The errors resulted from the determination of anisotropic interdiffusion coefficients can be analyzed by a robust treatment proposed by Lechelle et al [172], wherein the error propagation was considered in details. The method has been successfully applied to the diffusion study in many ternary systems [173,174]. Because the main purpose of this work is to present and demonstrate a high throughput methodology to extract the anisotropic interdiffusion coefficients, a simplified protocol was utilized to analyse the errors in the extracted interdiffusion coefficients $D_{\perp}(x)$ and $D_{\parallel}(x)$. By mainly considering the smoothing of the raw composition profile and the splitting the interdiffusion coefficients, the errors were estimated to be approximately 8%.

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Figure 4.8 Comparison between the experimental and calculated anisotropic interdiffusion coefficients of Mg-Al alloy at 673 K and 723 K. The dashed lines indicate that the difference between experimental and calculate values is within the range of a factor between 0.5 and 2.

Moreover, the magnitude of the anisotropic interdiffusion coefficient in Mg-Al alloy as a function of the Al content and orientation, $\tilde{D}(x, \theta)$ in various grain orientations at 673 K and 723 K could be calculated based on eq. (4-3). They are plotted in Figure 4.9a and Figure 4.9b, for 673 K and 723 K, respectively, together with experimental results obtained from the diffusion couples and show graphically the influence of Al content and orientation on the Al diffusion in the hcp Mg lattice.

Figure 4.9 Calculated interdiffusion coefficients as a function of the Al content and grain orientation according to eq. (4-3). (a) 673 K. (b) 723 K. Black circles stand for the experimental values obtained in the present work.

4.4.2 Anisotropic impurity diffusion coefficients

The Al impurity diffusion coefficients within the basal plane, $D_{Al}^{Mg}{}_{\perp}$, and along the c axis of the grain, $D_{Al}^{Mg}{}_{\parallel}$, could be extrapolated from the two interdiffusion coefficients along both orientations $D_{\perp}(x)$ and $D_{\parallel}(x)$ obtained in the present work when $x \rightarrow 0$. The Al impurity diffusion coefficients in hcp Mg along both orientations, extrapolated from the results in this work, are plotted as function of $1000/T$ (following the Arrhenius law) in Figure 4.10a, together with the experimental impurity diffusion coefficients obtained from Mg polycrystals [66–68,175] and single crystals along the basal plane and the c axis [95]. The present results are consistent with the experimental values obtained by Brennan [67] and Kammerer [66] using polycrystalline Mg-Al diffusion-couples and with the first principles calculations of Zhou [97]. Nevertheless, they are much smaller than those measured by Brennan [68] using the secondary ion mass spectrometry in polycrystalline Mg and by Das [95] using the diffusion couples in the single crystals. Brennan [68] already mentioned that the surface roughness introduced from the sputtering process could result in the artificial overestimation of the diffusion coefficients, which led to unreasonable higher values. Generally, these experimental values measured from the polycrystalline Mg are considered to be of mixed diffusion between the volume diffusion (itself varies with the distinct grain orientations) and grain boundary diffusion, i.e. essentially an average diffusion coefficient. Moreover, the experimental anisotropic impurity diffusion coefficients measured by Das [95], either within the basal plane or along the c axis, are even much higher than any of the previous values measured in the polycrystals [66–68], as shown in Figure 4.10a), which are considered to be controversial and not taken into account in the present work.

The Al impurity diffusion coefficients as a function of the grain orientation in pure hcp-Mg were successfully extrapolated at the dilute end of the Al content from the diffusion composition profiles. They are plotted in Figure 4.10b, together with the

4.4 Results and discussion

computed values based on eq. (4-3) when $x \rightarrow 0$. The experimental data from Das [93] at 673 K are also plotted in Figure 4.10b for comparison. They are almost one order of magnitude higher and, as discussed above, the results in the present work are more reliable and reasonable.

Figure 4.10 (a) The Arrhenius expression of the Al impurity diffusion coefficient in pure Mg. The different symbols stand for experimental results in the literature for polycrystals [66–68,175] and single crystals [95]. The solid lines stand for the predicted Al impurity diffusion coefficients perpendicular to the c axis, while the dashed lines represent the predictions along the c axis. Predictions from this investigation are shown as black lines while first-principles calculations are plotted as red lines [97]. (b) Influence of the rotation angle (θ) on the Al impurity diffusion coefficient at 673 K (black line), along with the experimental data from the present work (red squares) and Das *et al.* at 673 K (blue squares) [93].

4.4.3 Anisotropy ratio of the interdiffusion coefficients

The anisotropy ratio $D_{\perp}(x)/D_{\parallel}(x)$ between the interdiffusion coefficients along the basal plane and the c axis is widely used as an indicator of the anisotropy in diffusion process of the hcp materials. Regarding the self-diffusion coefficients of hcp materials, the anisotropy ratio correlates well with the c/a ratio of the lattice parameters. Experimental results of the self-diffusion anisotropy ratio show that

4.4 Results and discussion

$D_{\perp}/D_{\parallel} > 1$ in α -Ti [81], α -Zr [82], α -Hf [83] and Mg [88,89] with $c/a < \sqrt{8/3}$, whereas $D_{\perp}/D_{\parallel} < 1$ in Zn [84–86] and Cd [87] with $c/a > \sqrt{8/3}$. As for the self-diffusion hcp-Mg [88,89], the anisotropy ratio of the self-diffusion of the hcp Mg was 1.13 at 741 K and increased to 1.24 at 848 K [88], while $c/a = 1.6236 < \sqrt{8/3}$ [176], in good agreement with previous observations.

Regarding the impurity diffusion behavior, the anisotropy ratio $D_{\perp}(x)/D_{\parallel}(x)$ was found to be < 1 for some solute atoms (like Al, Zn, Y, and Gd [78,94,95,97]). Among them, the anisotropy ratio of the Al impurity diffusion coefficients was about 1.3 and decreased as the temperature increased [95]. They all show that the self-diffusion and impurity diffusion is faster within the basal plane.

Figure 4.11 (a) Evolution of the interdiffusion anisotropy ratio as a function of the Al content at 673 K and 723 K. (b) Evolution of the c/a ratio in hcp Mg with the Al content [176]. The variation of the lattice parameters a and c of hcp Mg with the Al content are shown in the inset.

The extraction of the anisotropic interdiffusion coefficients in this work also allows to evaluate the interdiffusion anisotropy ratio $D_{\perp}(x)/D_{\parallel}(x)$ as the function of the Al content in the hcp Mg-Al binary alloy. The variation of interdiffusion anisotropy ratio in hcp-Mg with the Al content at 673 K and 723 K is plotted in Figure 4.11a and $D_{\perp}/D_{\parallel} > 1$ over the entire Mg-Al composition range analyzed in this work.

4.5 Conclusions

Thus, interdiffusion was faster within the basal plane than along the c axis regardless of the Al content but the differences decreased as the Al content or the temperature increased, in agreement with the trends reported for the self-diffusion and Al impurity diffusion. The ratio extrapolated to the infinite dilute end of Al in hcp-Mg is about 1.48 at 673 K and ~ 1.37 at 723 K, similar to the reported anisotropy ratio 1.3 of the impurity diffusion of Al in hcp Mg [95]. The decrease of the interdiffusion anisotropy ratio is inherently associated with the change of the lattice parameters a and c (and, thus, the c/a ratio) with the Al content in the Mg-Al binary alloy [176], as depicted in Figure 4.11b. The increase of the Al content continuously reduced a and c , because Al has a negative size misfit with respect to the Mg host. But this reduction is larger for a in the basal plane, leading to an increase in the c/a ratio with the Al content, gradually approaching the ideal $c/a = 1.633$. Thus, the addition of Al solutes has a larger effect in the basal plane, leading to a larger solute-vacancy exchange barriers along this plane and reducing the interdiffusion component $D_{\perp}(x)$ within the basal plane, compared to $D_{\parallel}(x)$ along the c axis. Thus, the explanation of the change in the anisotropy of diffusion with the Al content follows from a consideration of the difference in the saddle points made by the introduction of Al in the hcp Mg lattice and thus the updated binding energy for diffusion in and out of the basal plane and the c axis [177]. Theoretically, the change of the configuration of the lattice by the increase of Al content in Mg-Al alloys also plays a key role in the formation vacancy energy in and out of basal plane, which requires further investigation.

4.5 Conclusions

The interdiffusion coefficients of Al in hcp Mg were extracted at 673 K and 723 K as a function of the grain orientation and Al content using a high-throughput experimental approach based on diffusion couples of polycrystalline samples. The

leakage of grain boundaries in the polycrystalline system was analyzed and was found to be negligible when the grain boundaries were perpendicular to the scanning route of the composition profiles. The minimum lateral distance between the scan lines and the grain boundaries to avoid grain boundary leakage was found to be around 40 μm in the Mg-Al alloy.

The anisotropic interdiffusion coefficients $D_{\perp}(x)$ and $D_{\parallel}(x)$, perpendicular and parallel to the c axis of the hcp Mg lattice, were determined as a function of the Al solute content from the experimental interdiffusion coefficients in grains with different orientation. $D_{\perp}(x)$ and $D_{\parallel}(x)$ increased with the Al content and the interdiffusion coefficients within the basal plane were 1.25 times and 1.15 higher than those along the c axis at 673 K and 723 K, respectively. The anisotropy factor $D_{\perp}(x)/D_{\parallel}(x)$ decreased with the Al content at both 673 K and 723 K. Finally, an explicit comprehensive expression of the interdiffusion coefficients as a function of Al content, grain orientation and temperature was derived. This information can be used as input in models of microstructure formation and solute redistribution resulting from such processes as solidification and precipitation, together with the crystallographic or thermodynamic anisotropy.

4.5 Conclusions

CHAPTER 5

Effect of solid solution on the strengthening for basal slip

5.1 Introduction

Micropillar compression tests in combination with high-throughput processing techniques based on the diffusion couples are used to ascertain the influence of solute atoms on the CRSS for basal slip in Mg-Al alloys at 298 K and 373 K. Micropillars with different dimensions are manufactured by the focus ion beam (FIB) technique and the size effects (and the associated deformation mechanisms) were analyzed in terms of solute content and temperature. It is found that the size effects impede the determination of the actual values of the CRSS at 298 K, but not at 373 K, because of the higher dislocation mobility that reduces the influence of the micropillar

5.2 Experimental procedure

dimensions on the deformation mechanisms.

5.2 Experimental procedure

Pure Mg and Mg-9 at.%Al alloys were manufactured by casting. They were used to produce Mg/Mg-9 at.%Al diffusion couples, which were annealed into quartz capsules in an Ar atmosphere at 673 K during 352 h to promote the diffusion of the solute atoms across the interface. The details of the manufacturing process can be found in section 2.1 and 2.2. The microstructure was characterized by EBSD in a dual beam scanning electron microscope (Helios Nanolab 600i FEI) to identify the grain orientation and grain size at an accelerating voltage of 30 kV and a beam current of 2.7 nA using a step size of 1.5 μm . The local composition analysis was performed by EPMA using Wavelength Dispersive Spectroscopy (WDS) in a JEOL Superprobe JXA-8900M, with a voltage of 20 kV and a beam current of 50 nA. The representative microstructure information across the interdiffusion region in the Mg-Al diffusion couples was indicated by the EBSD map as depicted in Section 4 in Figure 4.3. The grain size was quite large (around 1mm), and thus the micropillars for the mechanical characterization could be machined in the center of the grains, far from any grain boundary to avoid its effect. As detailed in the Section 4, there was a homogeneous composition gradient within the diffusion region, therefore various composition could be selected in the specific grain to study the solid solution strengthening.

Micropillars for mechanical characterization were milled in the grains suitably oriented for the basal slip with the following compositions: pure Mg, Mg-4.at%Al and Mg-9.at%Al alloys. The Schmid factors (SF) corresponding to basal slip and other deformation modes under the compression were computed for each selected grain, based on the grain orientation obtained from the EBSD measurements following the

5.2 Experimental procedure

protocol developed by Yang [178].

The first step is to convert the four-index Miller–Bravais indices of the plane ($h\ k\ i\ l$) and line direction [$u\ v\ t\ w$] to the standard three-index Miller–Bravais indices, ($h_n\ k_n\ l_n$) and [$u_n\ v_n\ w_n$], as indicated below:

$$d_{hkl} = [(2h + k)^2 + 3k^2 + 3l^2(a/c)^2]^{1/2} \quad (5-1)$$

$$d_{uvw} = [3(u + v/2)^2 + 9v^2/4 + w^2(c/a)^2]^{1/2} \quad (5-2)$$

$$\begin{bmatrix} h_n & u_n \\ k_n & v_n \\ l_n & w_n \end{bmatrix} = \begin{bmatrix} 2h + k/d_{hkl} & (2u + v)\sqrt{3}/2d_{uvw} \\ \sqrt{3}k/d_{hkl} & 3v/2d_{uvw} \\ \sqrt{3}l(a/c)/d_{hkl} & wc/ad_{uvw} \end{bmatrix} \quad (5-3)$$

where c and a are the lattice parameters of the hcp-Mg.

Afterwards, the Schmid factor (SF) is derived directly from the Euler angles $\{\varphi_1, \Phi, \varphi_2\}$ measured from the OIM analysis according to:

$$\text{SF} = \left| -\frac{h_n \sin \varphi_2 \sin \Phi + k_n \cos \varphi_2 \sin \Phi + l_n \cos \Phi}{\sqrt{(\sin \varphi_2 \sin \Phi)^2 + (\cos \varphi_2 \sin \Phi)^2 + \cos^2 \Phi} \times \sqrt{h_n^2 + l_n^2 + k_n^2}} \times \frac{u_n \sin \varphi_2 \sin \Phi + kv_n \cos \varphi_2 \sin \Phi + w_n \cos \Phi}{\sqrt{(\sin \varphi_2 \sin \Phi)^2 + (\cos \varphi_2 \sin \Phi)^2 + \cos^2 \Phi} \times \sqrt{u_n^2 + v_n^2 + w_n^2}} \right| \quad (5-4)$$

The calculated Schmid factors (SF) are employed to indicate the most likely deformation mechanism during micropillar compression tests. The Schmid factors employed in this section are provided in Table 5.1.

The high SF values for basal slip (> 0.45) in each alloy ensured that only basal slip was activated during the micropillar compression.

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Table 5.1 Schmid factor (SF) of the deformation modes under compression along the $[1\ 2\ \bar{3}\ 2]$, $[1\ 7\ \bar{8}\ 6]$ and $[\bar{5}\ 10\ \bar{5}\ \bar{6}]$ orientations for Mg, Mg-4 at.%Al and Mg-9 at.%Al alloys.

Deformation mode		Schmid factor (SF)		
		$[1\ 2\ \bar{3}\ 2]$	$[1\ 7\ \bar{8}\ 6]$	$[\bar{5}\ 10\ \bar{5}\ \bar{6}]$
Basal	(0001)[11 $\bar{2}$ 0]	0.47	0.45	0.25
	(0001)[1 $\bar{2}$ 10]	0.32	0.37	0.46
	(0001)[$\bar{2}$ 110]	0.15	0.08	0.21
Prismatic	(1 $\bar{1}$ 00)[11 $\bar{2}$ 0]	0.13	0.21	0.32
	(10 $\bar{1}$ 0)[1 $\bar{2}$ 10]	0.32	0.31	0.04
	(01 $\bar{1}$ 0)[$\bar{2}$ 110]	0.19	0.10	0.28
Pyramidal II	(11 $\bar{2}$ 2)[$\bar{1}$ 1 $\bar{2}$ 3]	0.33	0.12	0.07
	($\bar{1}$ 2 $\bar{1}$ 2)[1 $\bar{2}$ 13]	0.11	0.16	0.38
	(1 $\bar{2}$ 12)[$\bar{1}$ 2 $\bar{1}$ 3]	0.17	0.17	0.03
	($\bar{1}$ 1 $\bar{2}$ 2)[11 $\bar{2}$ 3]	0.10	0.28	0.16
	(2 $\bar{1}$ 1 $\bar{2}$)[$\bar{2}$ 113]	0.07	0.19	0.17
	($\bar{2}$ 112)[2 $\bar{1}$ 13]	0.44	0.12	0.03
{10 $\bar{1}$ 2} twin	(10 $\bar{1}$ 2)[$\bar{1}$ 011]	0.03	0.04	0.15
	(1 $\bar{1}$ 02)[$\bar{1}$ 101]	0.16	0.16	0.12
	(01 $\bar{1}$ 2)[0 $\bar{1}$ 11]	0.09	0.15	0.10
	(0 $\bar{1}$ 12)[01 $\bar{1}$ 1]	0.14	0.09	0.15
	($\bar{1}$ 012)[10 $\bar{1}$ 1]	0.02	0.08	0.15
	($\bar{1}$ 102)[1 $\bar{1}$ 01]	0.17	0.13	0.07

5.2 Experimental procedure

Micropillar compression tests were carried out using a Hysitron PI87 SEM Picoindenter within the scanning electron microscope (FEI Helios Nanolab 600) at 298 K (25 °C) as described in Section 2.5.2. The *in situ* tests were used to observe the formation and evolution of the slip traces along the lateral surface of the micropillar. The misalignment between the tip and the top surface of the pillars was carefully corrected in these tests. Micropillar compression tests were also performed at 373 K (100 °C) using a TI950 Triboindenter (Hysitron, INC., Minneapolis, MN), as stated in Section 2.5.2. Load was applied in all cases through a diamond flat punch with 10 μm in diameter. All the tests were implemented under displacement-control mode at an average strain rate of 10^{-3} s^{-1} up to a maximum strain of 10%. At least three tests were repeated for each condition (composition, size and temperature) to ensure the reproducibility of the results. The experimental load-displacement curves were primarily corrected by the Sneddon correction, and then converted to engineering stress (σ)-strain (ϵ) using the initial cross-sectional area and the height of the micropillars measured after the milling process, as described in Section 2.5.2. As the micropillar compression tests were performed in grains with different orientations, the results of the mechanical tests were plotted using the engineering resolved shear stress for basal slip, $\tau_{RSS} = \text{SF} \times \sigma$, where SF stands for the Schmid factor for basal slip in each case. The nano-indentation tests were carried in the bulk materials of the pure Mg and Mg-9. at%Al alloys under a constant strain rate 0.025 s^{-1} at the ambient temperature using the Hysitron TI950 Triboindenter system equipped with the Berkovich tip, as described in Section 2.5.1. All the tests were conducted in the load control mode with a loading and unloading time of 5 s, and 2 s holding time at maximum load of 12 mN.

The deformed micropillars were carefully examined using secondary electrons in the HR-SEM to observe the slip traces that appeared on the free surfaces. In addition, thin lamellas of $\approx 100 \text{ nm}$ in thickness were trenced and lifted-out from selected deformed micropillars by FIB, as shown in Section 2.4. They were subjected to

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transmission Kikuchi diffraction (TKD) to elucidate the crystal orientation after deformation and to ensure that the deformed micropillars did not suffer any twinning. The electron beam was operated at 15 kV with a beam current of 2.7 nA and the TKD maps were collected with a step size of 70 nm. Then, the transmission electron microscopy (TEM) was also employed to observe the dislocations after the deformation, at an accelerate voltage of 200 kV.

5.3 Experimental results

5.3.1 Mechanical response at room temperature (298 K)

The representative resolved shear stress (τ_{RSS})-strain (ϵ) curves corresponding to micropillars with different dimensions tested at room temperature for pure Mg, Mg-4 at.%Al and Mg-9 at.%Al alloys are plotted in Figure 5.1. The results of the micro-mechanical tests were consistent and the scatter was limited. The slope of the curve corresponding to the initial elastic region was always slightly lower than that associated with elastic unloading at the end of the test, regardless of the micropillar diameter. These differences could be attributed to the impossibility of attaining a completely perfect parallelism between the top surface of the pillar and the flat punch [179] even though large efforts were made to correct for the misalignment during the *in situ* tests. Despite this, the initial plastic yielding could be easily identified as discontinuities or changes in the initial slope in the resolved shear stress (τ_{RSS})-strain (ϵ) curves in all cases.

Regardless of the solute content, a pronounced size effect of the type “smaller is stronger” was found in all cases, in agreement with previous investigations [141,180,181]. The initial yield stress and flow stress of the $3 \times 3 \mu\text{m}^2$ micropillars were always substantially higher than that of larger micropillars, but the discrepancies

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in the flow stress between $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ were much smaller. However, substantial differences were found in the shape of the τ_{RSS} - ϵ curves as a function of solute content and pillar size, which indicated differences in the way the pillars deformed, as described in detail below.

Figure 5.1 Resolved shear stress (τ_{RSS}) vs. engineering strain (ϵ) curves for micropillars of different dimensions tested at ambient temperature. (a) Pure Mg; (b) Mg-4 at.%Al alloy and (c) Mg-9 at.%Al alloy.

In the case of pure Mg, basal slip was activated at very low stresses as seen from the beginning of the τ_{RSS} - ϵ curves (Figure 5.1a). This is not surprising considering the low CRSS values for basal slip in pure Mg at room temperature. Nevertheless, due to

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the annealing condition, the initial dislocation density is quite low and it is foreseen that the density of mobile dislocations will exhaust soon with the applied strain as dislocations gradually approach to the micropillar surface and suddenly scape out. Subsequently, the initial yield is followed by a hardening stage for $\varepsilon < 1\%$ that is more pronounced in the smaller pillar, especially for the $3 \times 3 \mu\text{m}^2$ micropillar. When the applied strain reaches 2%, strain bursts begin to appear in the resolved shear stress (τ_{RSS})-strain (ε) curves giving rise to the jerky behaviour typically found in micropillars deformation. They are represented by sudden drops in stress due to the loss of contact between the flat punch and the micropillar, and result from the sudden activation of dislocation sources at higher stresses. The magnitude of the strain bursts increases with the magnitude of the resolved shear stress (and thus, with the reduction in micropillar size), leading to large strain jumps in the micropillars with lateral dimensions of 3 and 5 μm , while the 7 μm micropillar displays a much smoother behavior. These observations agree well with the accepted theory of dislocation source exhaustion [148].

As the number of mobile dislocations exhausts, the applied stress reaches high enough values to activate new single arm dislocation that are statistically harder as the pillar size decreases. Once enough dislocation sources are activated for the further plastic deformation, the flow stresses seem to reach a plateau at large applied strains. The morphology of the deformed pillars shown in Figure 5.2 agree well with the described behavior. The orientation of the slip traces indicated the activation of basal slip in all cases, but the morphology of the slip traces differed with pillar size. Most of the plastic deformation in the $3 \times 3 \mu\text{m}^2$ micropillar of Figure 5.2a is concentrated in one slip band which corresponds to the large strain jump in Figure 5.2a. Deformation in the $5 \times 5 \mu\text{m}^2$ micropillar (Figure 5.2b) is localized in two slips bands (one more predominant than the other), associated with the strain bursts in the (τ_{RSS})-(ε) curves in Figure 5.2a. However, the surface of the largest $7 \times 7 \mu\text{m}^2$ micropillar presents many slips traces (Figure 5.2c), homogeneously distributed along the lateral surface of

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the deformed pillar, in agreement with a more continuous, less jerky behavior of the τ_{RSS} - ϵ curves, as depicted in Figure 5.1a. Nevertheless, the magnitude of the size effect between the $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ micropillars was negligible. These observations indicate that the behavior of the $7 \times 7 \mu\text{m}^2$ micropillar is less affected by the scarcity of dislocation sources since the larger pillar possesses a higher likelihood to contain more initial mobile dislocations, and hence should be close to be free of pillar size effects and resemble the bulk behavior.

Figure 5.2 SEM micrographs of the micropillars of pure Mg deformed up to $\approx 10\%$. (a) micropillar lateral dimension $3 \mu\text{m}$. (b) *Idem* $5 \mu\text{m}$. (c) *Idem* $7 \mu\text{m}$.

As the addition of solid solute atoms, similar size effects were also found in the (τ_{RSS}) - (ϵ) curves for Mg-4 at.%Al and Mg-9 at.%Al alloys, resulting from the dislocation source exhaustion, as demonstrated in Figure 5.1b and Figure 5.1c respectively, but there were significant differences observed in the shape of the resolved shear stress (τ_{RSS}) -strain (ϵ) curves as well as in the deformation behavior. For instance, contrary to pure Mg, a clear initial elastic region was found in the (τ_{RSS}) - (ϵ) curves for both Mg-Al alloys. This behavior indicates that the few available dislocations that are initially present in the micropillars are strongly pinned by the solute atoms and are not able to contribute to the plastic slip, especially for the higher solute contents. The presence of the solid solute atoms strongly hinders the glide and movement of the dislocations, and thus the applied stress should be increased to activate single-arm source to accommodate the further plastic deformation. It means

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the initial yielding in the Mg alloys is accomplished by the activation of single-arm dislocation sources, associated with the abrupt development of large strain bursts appeared in the $(\tau_{RSS})-(\epsilon)$ curves following the elastic region. The strain bursts are bigger as the pillar size decreases. The strain bursts are more pronounced for higher Al contents, for instance Mg-9 at%.Al alloy (Figure 5.1c), whilst the deformation behavior of Mg-4 at%.Al alloy (Figure 5.1b) is slightly similar to that of pure Mg.

Figure 5.3 SEM micrographs of the micropillars of Mg-9 at%.Al deformed up to $\approx 10\%$. (a) Micropillar lateral dimension $3\mu\text{m}$. (b) *Idem* $5\mu\text{m}$. (c) *Idem* $7\mu\text{m}$.

This behavior is in good agreement with the SEM micrographs of the deformed micropillars in all cases, for instance, those shown in Figure 5.3 for Mg-9 at%.Al alloy, that indicate that plastic deformation localizes in a few slip bands for all micropillar diameters. The evolution of slip traces during the compression process was observed during the *in-situ* micropillar compression tests for the $3\mu\text{m}$ and $7\mu\text{m}$ micropillars as shown in Figure 5.4 and Figure 5.5, respectively. The strain burst at strains around 1% are associated with the sudden formation of simultaneous basal slip bands in the small micropillar (Figure 5.4b) and the subsequent plastic deformation was localized in these slip bands, as depicted in Figure 5.4c. Plastic deformation in the $7\times 7\mu\text{m}^2$ micropillar was also discontinuous and took place by the progressive formation of slip bands of different intensity corresponding to successive strain bursts (Figure 5.5). Few basal slip bands appeared at the beginning of the deformation (Figure 5.5a) but the number increased with the applied strain. as denoted by the yellow and blue arrows in

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Figure 5.5b and Figure 5.5c, respectively. The plastic deformation mechanisms of the $5 \times 5 \mu\text{m}^2$ micropillar was intermediate between those found for the $3 \times 3 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ micropillars.

Figure 5.4 Development of basal slip traces in the $3 \mu\text{m}$ micropillars of Mg-9 at.% Al deformed *in situ* in the SEM at 25°C . (a) $\varepsilon = 1.2\%$. (b) $\varepsilon = 1.4\%$. (c) $\varepsilon = 10\%$.

All in all, the described behavior agrees well with the expected behavior for Mg micropillars favourably oriented for basal slip, but hinders the determination of solid solution strengthening effects from the tests. While it is possible to determine a yield stress for the Mg (Figure 5.1a) and Mg-4 at.% Al (Figure 5.1b) micropillars before the jerky behavior (characteristic of the operation of single arm dislocation sources) sets on, this is impossible for Mg-9 at.% Al alloy (Figure 5.1c), for which plasticity directly triggers with strain bursts associated with the activation of dislocation sources. It is speculated that the few mobile dislocations that are initially present in the micropillars are strongly pinned by the solute atoms and are not able to glide at room temperature before the jerky behavior sets on. This behavior could potentially be reverted by thermal activation, as shown below.

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Figure 5.5 Development of basal slip traces in the 7 μm micropillar of Mg-9 at.%Al deformed *in situ* in the SEM at 25 °C. (a) $\epsilon = 2\%$. (b) $\epsilon = 3\%$. (c) $\epsilon = 7\%$. The red arrows indicate the initial slip bands and the yellow and blue arrows denote the slip bands that gradually appeared at strains of 3% and 7%.

5.3.2 Mechanical response at 373 K

The representative resolved shear stress (τ_{RSS})-strain (ϵ) curves corresponding to the micropillars with different dimensions ($5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$) tested at 373 K (100 °C) for pure Mg, Mg-4 at.%Al and Mg-9 at.%Al alloys are presented in Figure 5.6. The curves showed a good repeatability and the scatter was limited. The general features of the resolved shear stress (τ_{RSS})-strain (ϵ) curves tested at 373 K (100 °C) were similar to those observed at ambient temperature, but some remarkable differences could be found in the way plasticity developed, especially for the Mg alloys with the higher solute content.

In the case of pure Mg (Figure 5.6a) and Mg-4 at.%Al alloy (Figure 5.6b), there is the an ignorable size effect on the initial yield stress and flow stress as the micropillar dimension reaches $5 \times 5 \mu\text{m}^2$. And also, the temperature has a negligible effect on the initial yield stress and flow stress compared to the curves obtained at ambient temperature (Figure 5.1b and Figure 5.1c). The flow stresses at large plastic strains and the magnitude of the strain bursts for micropillars of $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ are identical to those found at ambient temperature. The deformed micropillars also

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showed a strong localization of the deformation in slip bands at 373 K (100 °C), as shown in Figure 5.7.

Figure 5.6 Resolved shear stress and engineering strain curves obtained at 373 K (100 °C) for (a) pure Mg; (b) Mg-4 at.% Al; and (c) Mg-9 at.% Al. The high temperature compression tests were performed on micropillars with lateral dimensions of 5 μm and 7 μm.

In the case of Mg-9 at.% Al alloys (Figure 5.6c), however, notable differences in the resolved shear stress (τ_{RSS})-strain (ϵ) curves could be observed. The curves at 373 K (100 °C) also tend to reach a plateau in flow stress at large applied strains, at levels similar to those found at room temperature, but with a negligible size effect if the 5x5 μm² and 7x7 μm² micropillars are compared.

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Figure 5.7 SEM micrographs of the micropillars of the pure Mg deformed at 373 K up to $\approx 10\%$. (a) Micropillar lateral dimension $5\mu\text{m}$; (b) *Idem* $7\mu\text{m}$.

Moreover, the elastic to plastic transition is remarkably different to that found at room temperature (Figure 5.1c). First, the magnitude of the strain bursts is much smaller than that found at ambient temperature for the same micropillar size. Second, and as a result of the first, the initial yielding is much more gradual than that found at room temperature. Third, the deformation along the micropillars should be more homogeneous than that found at room temperature, and this hypothesis is supported by the SEM micrographs of the $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ Mg-9 at.%Al micropillars shown in Figure 5.8a and Figure 5.8b, respectively. Finally, the τ_{RSS} - ϵ curves presented in Figure 5.6 show evidence of serrated flow that can be attributed to the dynamic interaction between solute atoms and dislocations, namely Portevin-Le Chatelier (PLC) effect [182]. This mechanism (also named dynamic strain ageing) has also been reported for binary Mg alloys tested at high temperature [183,184], but not at room temperature [185], except for nanostructured binary Mg-Al alloys [186]. The results indicate that thermal activation helps overcome the pinning of the dislocations by the solute atoms in Mg-9 at.%Al, so that after the initial elastic loading, yielding takes place smoothly by the gliding of pre-existing basal dislocations, followed by the

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onset of the typical jerky behavior and the activation of single arm dislocation sources at larger stresses, similarly to what happens in pure Mg and Mg-4 at.%Al alloy at room temperature.

Figure 5.8 SEM micrographs of the micropillars of Mg-9 at.%Al alloy deformed at 373 K up to $\approx 10\%$. (a) Micropillar lateral dimension $5\mu\text{m}$; (b) *Idem* $7\mu\text{m}$.

In order to further ascertain the dominant deformation mechanisms in more detail, a thin foil was extracted from the deformed $7 \times 7 \mu\text{m}^2$ micropillar tested at 373 K (100 °C) in pure Mg and analyzed by the transmission EBSD and transmission electron microscopy (TEM), as illustrated in Figure 5.9. The SEM image of the deformed pillar is shown in Figure 5.9a, which also includes the orientation of the thin lamella extracted from the deformed micropillar. The yellow dashed line in Figure 5.9a indicates the position of the thin foil. The lamella was extracted along the vertical surface of the deformed micropillars, and included the whole longitudinal cross section of the micropillar and the inverse pole figure (IPF) obtained from the transmission EBSD analysis is presented in Figure 5.9b and shows only one orientation for the micropillar section after deformation. Thus, basal slip was the only active mechanism without any contribution from twinning.

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Figure 5.9 SEM micrograph of the 7 μm micropillar of pure Mg deformed at 373 K (100 °C). The yellow dashed line shows the orientation of the thin lamella extracted from the micropillar. (b) IPF figure of the lamella obtained from the EBSD measurement. (c) The dislocation analysis by the bright field TEM observation. The select area diffraction (SAD) was inserted. The zone axis in $[2\bar{1}10]$.

The dislocation structure in the deformed pillar was investigated by TEM as depicted in Figure 5.9c, and analyzed using the dislocation extinguish condition, as discussed in Chapter 2. The TEM lamellae was prepared with the zone axis of $[2\bar{1}10]$, and the diffraction vectors $[0002]$ and $[01\bar{1}0]$ were used to identify the Burgers vector of dislocations. Most of the deformation was carried by $\langle a \rangle$ dislocations along the basal slip bands. However, some dislocation segments and loops could also be observed in the prismatic plane between the basal slip bands. They might be created by cross-slip [187], which was not surprising since the Schmid factor for the prismatic

system was not zero. Moreover, the analysis of a thin foil extracted from a Mg-9 at.%Al micropillar tested at 373 K by TEM verified that the micropillars were free of precipitates after high temperature testing. It should be finally noted that the analysis of the lateral and top surfaces of the micropillars in the SEM before and after testing did not show any traces of oxidation.

5.4 Discussion

5.4.1 Factors influencing the initial plastic yielding of Mg alloys

The results presented above indicate that the initial yielding of Mg alloy micropillars favorably oriented for basal slip depends on a competition between the mobility of the pre-existing dislocations and the stress required to activate single-arm dislocation sources, which in turn depends on micropillar size and testing temperature. For low alloying contents (pure Mg and Mg-4 at.%Al), both at room temperature and 373 K, initial plastic yielding is smooth and progresses through the gliding of pre-existing dislocations at very low CRSS values. As the pre-existing dislocations escape out of the pillar surface for the smaller pillars ($3 \times 3 \mu\text{m}^2$), further elastic loading is required to the point at which large strain bursts start to develop associated with the activation of single arm dislocation sources, in agreement with the results in the literature [141,180]. Micropillars larger than $5 \times 5 \mu\text{m}^2$ are, however, less affected by size effects and display a smoother $\tau_{\text{RSS}}-\varepsilon$ curves. The observed behavior was different for high Al contents alloys. In this case, the pre-existing dislocations are strongly pinned by the solute atoms and initial plastic yielding at room temperature is dominated by the activation of single-arm dislocation sources even for the largest $7 \times 7 \mu\text{m}^2$ micropillar. Increasing the testing temperature up to 373 K, however, helps to overcome the pinning of the dislocations by the solute atoms in Mg-9 at.%Al alloys,

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so that after the initial elastic loading, yielding takes place smoothly by the gliding of pre-existing basal dislocations, reducing the magnitude of the size effect for 5×5 and $7 \times 7 \mu\text{m}^2$ micropillar.

Figure 5.10 The resolved shear stress τ_{RSS} - ϵ curves of micropillars of $5 \times 5 \mu\text{m}^2$ cross section of the Mg-9 at.%Al alloy. The red curve represents the deformation up to 2% at 373 K; the blue curve corresponds to the deformation of the same micropillar up to 10% at the ambient temperature after the 2% pre-deformation at 373 K. The black curve shows the mechanical response of the micropillar deformed up to 10% strain at the room temperature. The inset shows the localization of the plastic deformation in bands in the micropillar deformed at ambient temperature after pre-deformation at 373 K.

If this behavior is a result of the low initial density of mobile dislocations within the well-annealed pillars, a higher initial dislocation density should induce a less jerky behavior for the same pillar size at room temperature. This hypothesis was verified by the compression test in the micropillar with the dimension of $5 \times 5 \mu\text{m}^2$ in Mg-9 at.%Al alloys by pre-straining it at 373 K up to a strain of 2% to increase the dislocation density and re-testing it again at ambient temperature up to a strain of 10%. The corresponding τ_{RSS} - ϵ curves are plotted in Figure 5.10 and compared with that obtained at room temperature for Mg-9 at.%Al without pre-straining. At high temperature, the yielding was activated at lower initial yield stress compared to that at

room temperature, due to the thermal activation for the movement of dislocations. Indeed increasing the initial dislocation density reduced the magnitude of the strain bursts during deformation at room temperature and the resolved shear stress to deform the micropillar, confirming the initial hypothesis. The introduced dislocations from the pre-straining are also likely pinned by the solid solute atoms, and experience a similar deformation behavior as that in $7 \times 7 \mu\text{m}^2$ micropillar, containing higher density of initial existed dislocations. However, deformation was still jerky in nature and localized in a few shear bands (see inset in Figure 5.10). Thus, the initial dislocation density in the pre-strained pillar was not large enough to completely erase size effects at room temperature in Mg- 9 at.%Al alloy.

Figure 5.11 Load-displacement curves obtained from the nanoindentation tests in pure Mg and Mg-9 at.%Al alloys at ambient temperature. The insert shows the deformation behavior in the displacement range from 200 nm to 500 nm.

The strain bursts and jerky behavior were also found in the nanoindentation experiments carried out in bulk samples of pure Mg and Mg-9 at.%Al alloy. The load-displacement curves for both materials are plotted in Figure 5.11. The displacement jumps in the curve of the Mg-9 at.%Al alloy is typical of dynamic strain aging due to the interaction of solute atoms with dislocations. They do not appear in the case of

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pure Mg. The discrepancy in the load-displacement curves for both materials demonstrates the strong pinning effect of the solute atoms on the dislocation glide, since the dislocation density in both bulk materials is supposed to be comparable.

5.4.2 Determination of the solute strengthening for basal slip

The representative τ_{RSS} - ϵ curves at the ambient temperature and 373 K (100 °C) of the micropillars with $7 \times 7 \mu\text{m}^2$ cross section are plotted in Figure 5.12a and Figure 5.12b, respectively, for all the alloys to show more clearly the effect of the solute atoms on the mechanical response. The micropillar compression tests carried out at ambient temperature (Figure 5.12a) show the strengthening effect of the solute atoms, but it is not possible to determine the effect of the solute content on the actual CRSS because of the size effects encountered as explained in the previous section.

Figure 5.12 Resolved shear stress τ_{RSS} - ϵ curves of Mg, Mg-4 at.% Al, and Mg-9 at.% Al micropillars of $7 \times 7 \mu\text{m}^2$ cross section. (a) Ambient temperature. (b) 373 K (100 °C).

The size effect on the micropillar tested at 373 K (Figure 5.6) was significantly smaller than that found at ambient temperature, regardless of the solute content. In fact, plastic deformation was continuous from the beginning of the deformation for

Mg and Mg alloys in the micropillar with $7 \times 7 \mu\text{m}^2$ cross section, and a clear yield point could be identified at the beginning of the τ_{RSS} - ϵ curves in all cases. Even though the CRSS determined for pure Mg at the yield point (≈ 7 MPa) for micropillars with lateral dimensions of 5 and $7 \mu\text{m}$ was relatively higher than the value reported in the literature (below 1 MPa [14–16]), it seems reasonable to determine the influence of the solute content on the CRSS at 373 K as the difference in the CRSS at the initial yield point between the studied alloys and the pure Mg, $\Delta\tau$. The corresponding results are plotted in Figure 5.13 for Mg-Al alloys for the micropillars with lateral dimensions of $7 \mu\text{m}$.

Figure 5.13 The present experimental results of the solid strengthening Al on the increase of the CRSS, $\Delta\tau = \tau_{\text{alloy}} - \tau_{\text{Mg}}$, from compression tests in micropillars of $7 \times 7 \mu\text{m}^2$ cross-section at 373 K combined with the experimental data in the literature.

In order to validate the solute strengthening effects determined using micropillar compression, it is instructive to compare the results with previous works that used conventional bulk testing. Most past works to determine the CRSS for basal slip in Mg-Al alloys rely on the tensile testing of single crystals and belong to Akhtar and co-workers [42]. The results are plotted in Figure 5.13 for the sake of comparison. Both data at 25 °C and 100 °C are plotted in each case but are indistinguishable, as above

5.5 Conclusions

room temperature, solid solution strengthening enters the athermal regime [42]. Unfortunately, past fundamental studies in single crystals only covered dilute alloys, within the range of solubility at room temperature. No single crystal data could be found for supersaturated Mg-Al alloys, but Cáceres and Rovera [185] estimated the CRSS for basal slip from polycrystalline Mg-Al alloys and their data is also plotted in Figure 5.13 for the sake of comparison.

The strengthening due to the solid solution can be modeled using the Labusch model [188–190] according to:

$$\Delta\tau = \tau_{\text{alloy}} - \tau_{\text{Mg}} = Kc^{2/3} \quad (5-5)$$

where c is the solute element content (in at. %) and K is a constant that depends on the alloying element and temperature [188,190]. The experimentally determined strengthening slope in CRSS at 373 K correspond to $K = 1.4 \text{ MPa}^{-1}$ for supersaturated Mg-Al alloys. The results are in good agreement with the work of Cáceres and Rovera [185] and interestingly the strengthening slope K is the same as that for diluted Mg-Al alloys [42]. This suggests that random solid solution effects [190], which control the strengthening of dilute Mg-Al alloys, can be extrapolated to the supersaturation regime.

5.5 Conclusions

An experimental methodology based on the diffusion-couples and compression of micropillars has been developed to assess the influence of solute content and temperature on the CRSS values for the basal slip in Mg alloys. The micropillar compression tests at 298 K showed a large size effect (the smaller the stronger) associated with the limited number of mobile dislocations and the activation of single arm dislocation sources. The size effect led to the development of large strain bursts in

which deformation was localized in very few slips bands. These mechanisms were more noticeable as solute content increased, because of the pinning effect of solute atoms on dislocations, and, as a result, it was not possible to obtain size-independent values of the influence of the solute content on the critical resolved shear stress for basal slip.

Size effects were much smaller in micropillars tested at 373 K. Moreover, strain bursts almost disappeared for micropillars with a cross-section of $7 \times 7 \mu\text{m}^2$ and deformation by basal slip was fairly homogeneous along the micropillar length. These changes were attributed to the higher dislocation mobility at 373K. Under these circumstances, it was possible to estimate the contribution of the solute atoms to the critical resolved shear stress as the difference in the shear stress at the initial yield point between the alloys and the pure Mg micropillars. It was found that the solid solution strengthening provided by Al at 373 K followed the Labusch model and was in good agreement with previous experimental data obtained by bulk compression of single crystals.

5.5 Conclusions

CHAPTER 6

Effect of solid solution on the strengthening for tensile twinning

6.1 Introduction

As stated in Chapter 1, twinning plays a critical role in the plastic deformation in Mg and its alloys. Thus, understanding and strengthening twinning is of crucial importance to design Mg alloys with improved properties. In this chapter, micropillar compression tests are used in combination with diffusion couples to analyze the mechanisms of twin nucleation and growth in Mg-Al alloys. To this end, micropillars of cross-sections in the range $3 \times 3 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$ are milled from large grains with different Al content in the diffusion couples and are tested in compression along the $[01\bar{1}0]$ orientation. The CRSS values for twin nucleation and growth could be

6.2 Experimental procedure

obtained for the stress-strain curves after careful examination of the deformation mechanisms and of the effect of micropillar size. This information, together with the CRSS for basal from the previous investigation [191] and for pyramidal slip obtained from micropillar compression tests along [0001], show that the plastic anisotropy of Mg-Al alloys increased with the Al content.

6.2 Experimental procedure

The Mg/Mg-9 at.%Al diffusion couples analyzed in the previous chapter were used to study the effect of Al solute content on twinning. The microstructure characterization and composition analysis were performed following the same protocol. In this case, micropillars with a square cross-section with selected chemical compositions (pure Mg, Mg-4 at.%Al and Mg-9 at.%Al) were fabricated within the interdiffusion region in the center of grains oriented perpendicularly to the $[01\bar{1}0]$ orientation, which is favourable for tensile twinning activation. The cross section of the micropillars was varied from $3 \times 3 \mu\text{m}^2$ to $5 \times 5 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$ to explore the effect of the size on the mechanical behavior.

Micropillar compression tests were carried out using a TI950 Triboindenter (Hysitron, Inc., Minneapolis, MN) equipped with a diamond flat punch with a diameter of $15 \mu\text{m}$. All the tests were carried out at a constant strain rate of 10^{-3} s^{-1} under the displacement control up to a maximum strain of 10%. The engineering stress-strain curves were obtained from the corrected curves from the cross-sectional area and the height of the micropillar before deformation. At least three tests were repeated for each condition (alloy composition and micropillar size) to ensure the reproducibility of the results.

After the compression tests, the morphology of the deformed micropillars was

carefully examined using secondary electrons in the SEM. In addition, transmission-EBSD (*t*-EBSD) and transmission electron microscopy (TEM) were used to characterize the deformation mechanisms for selected micropillars. To this end, thin lamella of the cross-sections of the deformed micropillars were extracted using the standard lift-out technique in the FEI Helios 600 FIB microscope at 30 kV, as described in Section. 2.4.2. The *t*-EBSD mapping was carried out in the Helios Nanolab 600i FEI microscope equipped with an Oxford Instruments NordlysNano EBSD detector. The electron beam was operated at 15 kV with a beam current of 2.7 nA and the TKD maps were collected with a step size of 50 nm. The TEM observations were performed in Talos F200X microscope at an accelerating voltage of 200 kV.

6.3 Experimental results

6.3.1 Deformation mechanisms of pure Mg during $[01\bar{1}0]$ compression

The micropillars were deformed parallel to the $[01\bar{1}0]$ orientation of the Mg lattice. The experimental values of the CRSS for different deformation modes of pure Mg under compression in the literature [14–18,39] are summarized in Table 6.1, together with the corresponding Schmid factors (SF) for compression along the $[01\bar{1}0]$, $[01\bar{1}6]$ and $[0001]$ orientations. The second orientation corresponds to the lattice orientation after $\{10\bar{1}2\}$ tensile twinning, while $[0001]$ direction was selected to study pyramidal slip. The Schmid factor for all the slip systems and tensile twinning were computed based on the crystal orientation information obtained from the EBSD measurements following the protocol in [178].

6.3 Experimental results

Table 6.1 Critical resolved shear stress (CRSS) and Schmid factor (SF) of the possible deformation modes in Mg under compression along the $[01\bar{1}0]$, $[01\bar{1}6]$ and $[0001]$ orientations. The $[01\bar{1}6]$ orientation corresponds to the crystal orientation after twinning.

Deformation mode		CRSS (MPa)	Schmid factor (SF)		
			$[01\bar{1}0]$	$[01\bar{1}6]$	$[0001]$
Basal	$(0001)[11\bar{2}0]$	0.5 [14–16]	0	0.13	0.03
	$(0001)[1\bar{2}10]$		0	0.12	0.05
	$(0001)[\bar{2}110]$		0	0.02	0.02
Prismatic	$(1\bar{1}00)[11\bar{2}0]$	39 [17]	0.46	0.01	0
	$(10\bar{1}0)[1\bar{2}10]$		0.39	0.01	0
	$(01\bar{1}0)[\bar{2}110]$		0.07	0	0
Pyramidal II	$(11\bar{2}2)[\bar{1}\bar{1}23]$	80 [18]	0.27	0.49	0.43
	$(\bar{1}2\bar{1}2)[1\bar{2}13]$		0.32	0.48	0.43
	$(1\bar{2}12)[\bar{1}2\bar{1}3]$		0.39	0.38	0.47
	$(\bar{1}\bar{1}22)[11\bar{2}3]$		0.34	0.37	0.46
	$(2\bar{1}\bar{1}2)[\bar{2}113]$		0	0.44	0.45
	$(\bar{2}112)[2\bar{1}\bar{1}3]$		0.37	0.07	0.16
{10 $\bar{1}2$ } twin	$(10\bar{1}2)[\bar{1}011]$	12 [39]	0.09	0.48	-0.49
	$(1\bar{1}02)[\bar{1}101]$		0.15	0.49	-0.49
	$(01\bar{1}2)[0\bar{1}11]$		0.49	0.47	-0.50

6.3 Experimental results

$(0\bar{1}12)[01\bar{1}1]$	0.48	0.49	-0.49
$(\bar{1}012)[10\bar{1}1]$	0.09	0.49	-0.49
$(\bar{1}102)[1\bar{1}01]$	0.15	0.48	-0.50

Although the CRSS for basal slip is very low (≈ 0.5 MPa), this mechanism is not expected to be dominant in the micropillar oriented along the $[01\bar{1}0]$ orientation because the Schmid factor for basal slip is almost zero. $\{10\bar{1}2\}$ tensile twinning shows the highest Schmid factor (0.48 - 0.49), followed by prismatic slip (0.46). However, the CRSS for prismatic slip is much higher than that of tensile twinning and, therefore, $\{10\bar{1}2\}$ tensile twinning is expected to be the preferred deformation mode under $[01\bar{1}0]$ compression. It is worth noting that two twin variants have very high Schmid factors and, thus, they have similar probabilities to develop during deformation.

After twinning, the loading axis changes to the $[01\bar{1}6]$ orientation in the twinned region as a result of the crystal reorientation by $\sim 86^\circ$, which is schematically shown in Figure 6.1. The new compression direction has a misorientation $\sim 5^\circ$ with respect to $[0001]$ crystal orientation [53,187], and the Schmid factors for all deformation modes in the twinned region are listed in Table 6.1. Since the new compression axis is quite close to the $[0001]$ orientation, the active deformation mechanisms is likely to be similar to the ones found during compression along the $[0001]$ orientation [187,192,193].

6.3 Experimental results

Figure 6.1 Schematic of the orientation relationship between the parent and twin regions in the micropillar. The parent crystal is reoriented by $\sim 86^\circ$ by twinning.

A representative engineering stress-strain curve is plotted in Figure 6.2 from the compression test of a micropillar of pure Mg of $5 \times 5 \mu\text{m}^2$ cross-section. The initial linear elastic response is abruptly finished by an abrupt load drop followed by a strain burst. Afterwards, the deformation progresses at constant stress up to an applied strain of 5.5% when the micropillar shows a very high strain hardening up to the maximum applied strain of 10%. The different regions in the stress-strain curve are expected to correspond to different dominant deformation mechanisms and, thus, various tests were stopped at after the first load drop ($\epsilon \approx 1\%$), at the end of the plateau region ($\epsilon \approx 6\%$) and $\epsilon \approx 10\%$ to analyze the microstructure. The corresponding points are marked with (b), (c) and (d), respectively, in Figure 6.2a.

The observation of the micropillar in the SEM after the sudden load drop at 1% strain (Figure 6.2b) showed a slight tilt along the edge of the lateral surface (marked with an arrow). A thin lamella was extracted from the deformed micropillar and characterized by *t*-EBSD. This analysis showed that the two variants of the $\{10\bar{1}2\}$ twin (T1 and T2) with the highest Schmid factor were nucleated in the upper part of

the micropillar (Figure 6.2e), leading to a $\sim 86^\circ$ rotation from the parent lattice. The crystal orientation of both twinning variants and of the parent are schematically shown in Figure 6.2h. The twin boundary (TD) and the boundary between the two twin variants (TTB) were marked by black and yellow lines, respectively, in Figure 6.2e. Thus, the load drop was associated with the crystal reorientation induced by the nucleation of two $\{10\bar{1}2\}$ twin variants.

After twin nucleation, the flow stress remains constant up to an applied strain of $\approx 5.5\%$. The SEM micrograph of another micropillar deformed up to 6% shows that the tilt feature along the lateral edge has propagated up to the bottom of the micropillar (Figure 6.2c) and the orientation map obtained by *t*-EBSD of another lamella extracted from the micropillar is shown in Figure 6.2f. It confirmed that the whole micropillar was twinned by the thickening of both twin variants that took place at constant stress.

Another micropillar was tested up to an applied strain of 10%. The SEM micrograph of the deformed micropillar showed the presence of slip traces parallel to the basal plane of the twinned crystal on the lateral surface (Figure 6.2d). Although the orientation within the twinned region is not favourably oriented for basal slip ($\sim 8^\circ$ misorientation with respect to the *c*-axis), slip traces were found on the lateral surface of the micropillar (Figure 6.2d) because the applied stress was very large (close to 400 MPa) and the CRSS for basal slip is quite low.

6.3 Experimental results

Figure 6.2 (a) Representative engineering stress-strain curve of a pure Mg micropillar of $5 \times 5 \mu\text{m}^2$ deformed in compression along the $[01\bar{1}0]$ orientation. (b) SEM micrograph of the deformed micropillar after the load drop at $\sim 1\%$ strain. (c) *Idem* at 6% strain. (d) *Idem* at 10% strain. (e-f) *t*-EBSD maps of a thin lamella extracted from the deformed micropillars in (b-c). (g) Schematic of the HCP lattice orientation in both twin variants and in the parent crystal. Black and yellow lines in (e-f) stand for the twin boundary (TD) and the boundary between the two twin variants (TTB).

Figure 6.3 TEM micrographs of lamella extracted from micropillars deformed up to different strains. (a) Applied strain 6%. $\langle a \rangle$ dislocations in the prismatic plane within the parent region, $g=[01\bar{1}1]_p$. (b) Applied strain 6%. $\langle c \rangle$ dislocations in the twinned region, $g=[0002]_t$. (c) Applied strain 10%. $\langle c \rangle$ dislocations in the twinned region, $g=[0002]_t$. (d) Same as (c) but observed under the $g=[01\bar{1}1]_t$, confirming the presence of $\langle a+c \rangle$ dislocations in this region. The zone axis was $[2\bar{1}\bar{1}0]$ in all cases.

In order to further investigate the deformation mechanisms, the lamella extracted from the micropillars deformed up to 6% and 10% were examined by TEM. A reduced number of $\langle a \rangle$ dislocations are observed within the parent crystal on the prismatic plane in the micropillar deformed up to 6%, as shown in Figure 6.3a under the diffraction condition of $g=[01\bar{1}1]_p$. Although the CRSS value for prismatic slip is

6.3 Experimental results

very high (Table 6.1), it is possible that prismatic slip was activated taking into account the compressive stress attained to nucleate the twin and the Schmid factor of some prismatic slip systems [187,194]. Nevertheless, their contribution to the plastic slip should be small taking into account the small density of these dislocations. A few dislocations were also observed on non-basal planes in the vicinity of the twin boundary within the twinned region with a $\langle c \rangle$ component when the applied strain was 6% (Figure 6.3b). At the $g=[0002]_t$ diffraction condition, the visible dislocations have a Burgers vector with a $\langle c \rangle$ component based on the dislocation extinction criterion, and they may be $\langle c \rangle$ or $\langle c+a \rangle$ dislocations. The density of these dislocations increased dramatically when the applied strain reached 10%, as shown in Figure 6.3c. When the diffraction condition is changed to $g=[01\bar{1}1]_t$, dislocations containing an $\langle a \rangle$ component could be revealed and more dislocations are observed under $g=[01\bar{1}1]_t$ in Figure 6.3d, confirming the presence of the dislocations with Burgers vector $\langle c+a \rangle$. The large density of $\langle c+a \rangle$ dislocations in the prismatic plane within the twinned region, associated to the large strain hardening of the stress-strain curve, indicates that pyramidal slip was progressively activated within the twinned micropillar for applied strains $> 6\%$ and become the dominant plastic deformation mechanism once the whole micropillar was twinned.

The twin nucleation stress was determined from the critical point of load drop (associated with the formation of twin), while the twin growth stress was corresponding to the stress-plateau that was associated with the migration of the twin boundaries, as stated above. The magnitude of the critical stresses for twin nucleation and growth are consistent with the results of Wang. et. al [53], who tested in compression Mg micropillars oriented for twinning. Some of the micropillars were twin-free while others contained twins and thus, the critical stresses for twin nucleation and growth were determined in different micropillars. In our case, both magnitudes were determined from a single test in a twin-free micropillar.

6.3.2 Deformation mechanisms of Mg-Al alloys during $[01\bar{1}0]$ compression

A representative engineering stress-strain curve of a micropillar of $7 \times 7 \mu\text{m}^2$ is plotted in Figure 6.4a for a Mg-9 at.%Al alloy. The micropillar was milled in another grain with the same $[01\bar{1}0]$ orientation and the general features of the curve were similar to those reported for pure Mg (Figure 6.2a). A pronounced load drop accompanied by a strain burst took place after elastic deformation up to 1% strain. Deformation progressed at constant stress afterwards, followed by a step hardening region for strains $> 5\%$. The stress carried by the micropillar at 10% was close to 600 MPa, much higher than the one in the case of pure Mg (≈ 400 MPa). Moreover, strain bursts (that can be noticed by sudden drops in the load during deformation) were found in the plateau and hardening regions of the Mg-9 at.%Al alloy but not in the case of the pure Mg micropillars.

Micropillar compression tests were stopped at 1% strain, after the sudden load drop, and at 10% strain to further analyze the deformation mechanisms. The micropillar deformed up to 1% showed a slight tilt along the edge of the lateral surface (Figure 6.4b), as in the case of pure Mg. A thin lamella was extracted from the micropillar and characterized by TEM. The twinned region occupied the upper part of the whole pillar, and two TBs can be found in Figure 6.4d. They were parallel to the twin plane, indicated by the red dotted line. Moreover, the TTB between the two $\{10\bar{1}2\}$ twin variants (T1 and T2) is marked by the yellow dashed line in Figure 6.4d. The presence of the twin and of the parent were explicitly confirmed by the diffraction patterns.

6.3 Experimental results

Figure 6.4 (a) Representative engineering stress-strain curve of a Mg-9 at.%Al micropillar of 7x7 μm^2 deformed in compression along the $[01\bar{1}0]$ orientation. (b) SEM micrograph of the deformed micropillar after the load drop at $\sim 1\%$ strain. (c) *Idem* at 10% strain. (d) TEM micrograph of the thin lamella extracted from the micropillar in (b), including the diffraction patterns of the parent and twin regions. (e) *t*-EBSD maps of a thin lamella extracted from the micropillar in (c). Black and yellow lines stand for the twin boundary (TD) and the boundary between the two twin variants (TTB). (f) Schematic of the HCP lattice orientation in both twin variants and in the parent crystal.

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The lateral surface of the micropillar deformed up to 10% also showed slip traces parallel to the basal plane of the twinned crystal (Figure 6.4c). The *t*-EBSD image of a lamella extracted from this micropillar showed that the whole micropillar has been twinned and one of the twin variants has propagated and replaced the other variant (Figure 6.4e), which was only found at the bottom-right corner of the micropillar. The crystal orientation of the twin variants and of the parent are shown in Figure 6.4f. Similar to the case of pure Mg, one twin variant grew at the expense of the other variant during deformation. The slip traces and the slip steps corresponding to the basal plane in the twinned crystal were more marked than in pure Mg (Figure 6.4c) and they could account for the strain bursts during strain hardening.

Figure 6.5 (a) Applied strain 1% *<a>* dislocations in the prismatic plane within the parent

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region, $g=[01\bar{1}1]_p$. (b) Applied strain 1%. $\langle c \rangle$ dislocations in the twinned region, $g=[0002]_t$. (c) Applied strain 10%. $\langle c \rangle$ dislocations in the twinned region, $g=[0002]_t$. The zone axis was $[2\bar{1}\bar{1}0]$ in all cases.

The dislocation structure within the parent and twinned regions was analysed by TEM. Prismatic $\langle a \rangle$ dislocations in the parent region (Figure 6.5a) as well as pyramidal $\langle a+c \rangle$ dislocations in the twinned region (Figure 6.5b) were found in the micropillar deformed up to 1%, as in the case of pure Mg. The density of pyramidal $\langle c+a \rangle$ dislocations in the twinned region increased when the micropillar was deformed up to 10% (Figure 6.5c) but the dislocation density was significantly lower than in the case of pure Mg. These differences are obviously related to the higher strain hardening of the Mg-9 at.%Al micropillars and they will be analyzed in more detail below.

6.3.3 Size effects during $[01\bar{1}0]$ compression of Mg and Mg-Al alloys

The engineering stress-strain curves of the compression tests of micropillars of pure Mg, Mg-4 at.%Al and Mg-9 at.%Al with different lateral cross-section (in the range $3 \times 3 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$) are plotted in Figure 6.6a, Figure 6.6b and Figure 6.6c, respectively. The three regions analyzed in the previous sections were found in all cases, regardless of the micropillar size and Al content. The critical stress for twin nucleation was higher in the $3 \times 3 \mu\text{m}^2$ micropillars but no differences were found between $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ micropillars. The constant stress plateau after twin nucleation, that was associated to the propagation of one dominant twin variant, was again slightly higher in the $3 \times 3 \mu\text{m}^2$ micropillars of pure Mg, as compared with larger micropillars. However, these differences were not found in the Mg-Al micropillars. Finally, a size effect was also found in the strain hardening region for applied

6.3 Experimental results

strains $>5\%$ in the case of $3 \times 3 \mu\text{m}^2$ micropillars of Mg and Mg-Al alloys. However, no significant differences were found in the strain hardening of the larger micropillars. It should also be noticed that the macroscopic shape of the micropillars after testing was independent of the micropillar size and Al content. Slip traces parallel to the basal plane of the twinned crystal were always present (Figure 6.7) and it indicates that the dominant deformation mechanisms were not modified by the micropillar dimensions.

Figure 6.6 Representative engineering stress-strain curves of micropillar compression tests along $[01\bar{1}0]$ direction in micropillars with lateral cross sect in the range $3 \times 3 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$. (a) Pure Mg, (b) Mg-4 at.%Al alloy and (c) Mg-9 at.%Al alloy.

Figure 6.7 SEM micrographs of the $5 \times 5 \mu\text{m}^2$ micropillars deformed up to 10%. (a) pure Mg, (b) Mg-4 at.%Al alloy and (c) Mg-9 at.%Al alloy. Slip traces along the basal plane of the twinned region are indicated by the red dash lines.

6.4 Discussion

6.4.1 Effect of the micropillar size on the CRSS for twin nucleation and growth

It is well-known that critical stress for dislocation slip [145,180,181,187,191,192] as well as twin nucleation and growth [53,141,200,180,181,187,195–199] increase as the micropillar size decrease. Thus, the analysis of this size effect is mandatory to assess the ability of the micropillar compression tests to provide accurate information about the influence of the solute atoms on the critical stress for twin nucleation and growth. The average values and standard deviation of the critical shear stresses for $\{10\bar{1}2\}$ twin nucleation τ_n , and growth τ_g , for pure Mg, Mg-4 at.%Al and Mg-9 at.%Al alloys are plotted as a function of micropillar size in Figure 6.8a and Figure 6.8b, respectively. The twin nucleation stress (τ_n) is defined as the resolved shear

stress on the twin plane at the peak stress associated to the twin nucleation. The twin growth stress (τ_g) stands for the shear stress resolved on the twin plane in the beginning of the plateau region, after the load drop due to the strain burst associated with the nucleation of the twin.

Figure 6.8 (a) CRSS for twin nucleation (τ_n) as a function of the micropillar lateral dimension and Al content. (b) CRSS for twin growth (τ_g) as a function of the micropillar lateral dimension and Al content. (c-d) Effect of micropillar dimension on the CRSS for twin nucleation and growth for pure Mg. Results from this investigation and from the literature [53,141,180,181,187,195].

A size effect of the type ‘smaller is stronger’ was found in the CRSS for twin nucleation in the micropillars of $3 \times 3 \mu\text{m}^2$ of Mg and Mg-9 at.%Al. Nevertheless, the

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values of τ_n were similar for micropillars of $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$, regardless of the Al content. In the case of the CRSS for twin growth, a size effect was only found in the micropillars of $3 \times 3 \mu\text{m}^2$ of Mg-9 at.%Al and no significant differences in τ_g were found for Mg and Mg-4 at.%Al as a function of the micropillar dimensions. In the case of pure Mg, the experimental values of τ_g and τ_n have been plotted in Figure 6.8c and Figure 6.8d as a function of the micropillar lateral dimension together with those available in the literature. They show large differences in the critical stress values among different investigations but the size effects for both twin nucleation and growth are normally limited to micropillars with lateral dimensions below $3 \mu\text{m}$. The large differences in the CRSS can be attributed to the localized nature of the twin nucleation, which is triggered at the contact point between the flat punch and the micropillar upper surface. Small misalignments (which are very difficult to correct) can lead to large differences in the measured critical stress. Overall, the experimental data for pure Mg obtained in this investigation are consistent with most of the results in the literature.

6.4.2 Effect of Al content on the CRSS for twin nucleation and growth

As the effect of the micropillar dimensions on the critical shear stress for twin nucleation and growth was negligible for micropillars of $5 \times 5 \mu\text{m}^2$ and $7 \times 7 \mu\text{m}^2$ cross-section, the values measured with the latter were used to assess the effect of Al content on them. They are plotted in Figure 6.9a and the CRSS for twin nucleation approximately 80 MPa higher than that for twin growth, regardless of the Al content. The hardening contribution due to the presence of Al atoms in the CRSS for twin nucleation and growth, expressed as below, is plotted in Figure 6.9b.

$$\Delta\tau_n = \tau_n(\text{Al}) - \tau_n(0) \quad (6-1)$$

$$\Delta\tau_g = \tau_g(\text{Al}) - \tau_g(0) \quad (6-2)$$

where $\Delta\tau_n$ and $\Delta\tau_g$ represent the increase in CRSS for twin nucleation and growth.

Figure 6.9 (a) CRSS for twin nucleation, τ_n , and growth, τ_g , measured in micropillars of $7 \times 7 \mu\text{m}^2$ cross-section as a function of Al content. (b) Increase of the CRSS for twin nucleation τ_n , and growth τ_g , as a function of the Al content. Experimental data of the increase of CRSS for basal slip [191] and the first-principle predictions of the effect of Al content on the CRSS for twin growth [201] and basal slip [202] are also plotted for comparison.

Twin thickening is a process mediated by the propagation of twinning dislocations and the solute strengthening was analyzed by Ghazisaeidi et al. [201] using a modified version of Labusch model [203] that takes into account that a straight dislocation bows out in the glide plane to minimize the potential energy in the presence of a random solute distribution. The interaction energy between the solute atoms with the twin dislocation (and also with the twin boundary) was determined from first principles calculations, leading to a linear dependence of the CRSS with the Al content for a given value of the strain rate and temperature. The difference with the traditional Labusch model, that predicts that the yields scales with the solute atom concentration to the power of $2/3$, is due to the small Burgers vector of the twinning dislocation and to the solute-twin boundary interaction, that provides the main

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contribution to the strengthening. The predictions obtained from eq. (8) in [201] for ambient temperature and a strain rate of 10^{-3} s^{-1} are plotted in Figure 6.9b. They are in good agreement with the experimental results for Mg-4 at.%Al but underestimate the experiments for Mg-9 at.%Al. The origin of these differences may be found in that the energy interaction between the solute atoms and the twin dislocation and the twin boundary was calculated using a dilute approximation, that might not be accurate when the Al content is 9 at.%.

The recent experimental data of the influence of Al content on the CRSS for basal slip $\Delta\tau_b$ [191], obtained using the same experimental approach, have been plotted in Figure 6.9b as well, together with the predictions from [202] based on the modified Labusch model. The agreement between experiments and simulations is good up to 4 at. %Al and the extrapolation of the model to the non-dilute range also seems to be in agreement with the experimental results in the case of basal slip. Moreover, both experimental and simulations show that the strengthening provided by Al solute atoms is higher in the case of twin nucleation and growth than in the case of basal slip.

6.4.3 Strain hardening in the twinned micropillars

The stress-strain curves of the micropillars oriented for twinning showed a region with strong strain hardening when the applied strain was higher than 5%. Similar behaviour has been reported during micropillar compression [141,181] as well as uniaxial [204] and plane strain compression [9] Mg and Mg alloys single crystals oriented for twinning. The origin of the strain hardening has been attributed to the activation of $\langle a+c \rangle$ pyramidal slip to accommodate the deformation in the twinned crystal, which is not suitable oriented for basal slip. Moreover, other authors also pointed out the strengthening may also be caused by the presence of TTB which may block dislocation slip [181]. It should also be noted that the strain hardening rate

increased rapidly with the Al content for all micropillar sizes.

Figure 6.10 Representative resolved shear stress – strain curves of micropillars of 5×5 and $7 \times 7 \mu\text{m}^2$ cross-section of Mg-4 at.%Al, and Mg-9 at.%Al. (b) CRSS to activate pyramidal dislocation slip in Mg, Mg-4 at.%Al and Mg-9 at.%Al. The results for pure Mg are obtained from [187,192].

After twinning, the compression direction was close to the c -axis and new micropillar compression tests were carried out in specimens of Mg-4 at.%Al and Mg-9 at.%Al alloys oriented in $[0001]$ direction. There are 5 equivalent pyramidal slip systems in this orientation with high Schmid factors (between 0.46 and 0.43, see Table 6.1) which are similar to those in the $[01\bar{1}6]$ orientation within the twinned region of the micropillars in Figure 6.6 (between 0.37 and 0.49 in Table 6.1). Three tests were carried out for each alloy in micropillars of $7 \times 7 \mu\text{m}^2$ cross-section to ascertain the CRSS for $\langle a+c \rangle$ pyramidal slip as a function of the Al content. They were not performed in pure Mg because the CRSS for pyramidal slip was well established from previous studies [187,192]. Two representative resolved shear stress–strain curves obtained from these experiments are plotted in Figure 6.10a. The initial response is elastic followed by a plastic region with linear strain hardening. This behaviour is equivalent to that found in pure Mg deformed in compression along the $[0001]$ direction [187,192]. The analysis of the deformed micropillars in the SEM showed the presence of slip traces parallel to the basal plane (Figure 6.11a), very similar to those

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found in the micropillars tested along $[01\bar{1}0]$ after twinning (Figure 6.7). The *t*-EBSD map of a thin lamella extracted from that deformed pillar of Mg-4 at.%Al did not show any evidence of twinning (Figure 6.11b), indicating that the plastic deformation was accommodated by dislocation slip.

Figure 6.11 (a) SEM micrograph of the Mg-4 at.%Al micropillar deformed along the $[0001]$ direction. (b) *t*-EBSD maps of a thin lamella extracted from the micropillar in (a). (c) TEM micrographs of that lamella under the condition $g=[0002]$ to reveal the $\langle c \rangle$ dislocations. (d) Same as (c) observed under $g=[01\bar{1}0]$ to reveal $\langle a \rangle$ dislocations.

The CRSS for the initiation of plastic slip could be easily computed from the onset of non-linear deformation in Figure 6.10a and the average values (as well as the standard deviation) are plotted in Figure 6.10b as a function of the Al content. The experimental results in the case of pure Mg included in Figure 6.10b are taken from [187,192]. The dislocation structure in the deformed micropillars was analysed by TEM. As found within the twin region of the micropillars deformed along $[01\bar{1}0]$, $\langle a \rangle$ prismatic dislocations as well as $\langle a+c \rangle$ pyramidal dislocations were found under the

diffraction conditions $g = [0001]$ (Figure 6.11c) and $g = [01\bar{1}0]$ (Figure 6.11d), respectively. Thus, plastic deformation along $[0001]$ was mainly accommodated by the pyramidal slip, and the influence of the Al content on the CRSS for pyramidal slip can be found in Figure 6.10b.

The presence of solute atoms increased dramatically the CRSS for pyramidal slip ($\tau_p \approx 98$ MPa in pure Mg to $\tau_p \approx 250$ MPa in Mg-9 at.%Al) and these differences may explain the effect of the Al content of the strain hardening rate of the micropillars deformed along $[01\bar{1}0]$ after twinning. In the case of pure Mg, plastic deformation by pyramidal slip is activated when the CRSS on the pyramidal system reaches around 100 MPa, and this stress level is attained at low strains when the applied engineering stress in the micropillar reaches ≈ 200 MPa ($\approx 6\%$ in Figure 6.6a). Thus, most of the strain hardening of the twinned Mg micropillar up to 10% strain is associated with the interaction between pyramidal dislocations and also the interaction of pyramidal dislocations with TTB [187,192]. Activity of pyramidal dislocations was very large under these conditions, as shown in Figure 6.3c and Figure 6.3d. Nevertheless, the CRSS to activate pyramidal slip in the twinned Mg-9 at.%Al micropillars was much higher (250 MPa) and compressive stress higher than 500 MPa were necessary to promote pyramidal slip. These stresses were only achieved at very high strains ($> 8\%$) in the micropillars with 5×5 and $7 \times 7 \mu\text{m}^2$ cross-section. Thus, in the absence of pyramidal slip and with very limited basal slip activity, the deformation has to be partially accommodated by elastic strains, leading to very large strain hardening rates in the Mg-Al alloys, as compared with pure Mg. This mechanism was confirmed by limited presence of $\langle a+c \rangle$ pyramidal dislocations in the Mg-Al micropillars after 10% strain (Figure 6.5b and Figure 6.5c).

6.5 Conclusions

The effect of Al content on the critical resolved shear stress for twin nucleation and growth was analysed by the combination of diffusion couples with micropillar compression tests. Micropillars of square cross cross-sections in the range $3 \times 3 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$ were deformed along $[01\bar{1}0]$. The deformation mechanisms were independent of the micropillar dimensions and Al content. The stress for twin nucleation was identified by a sudden strain burst due to the nucleation of one or two twin variants in the upper region of the micropillar. Afterwards, twin propagation occurred at a constant stress until the whole micropillar was twinned and deformation was partially accommodated by deformation of the twinned micropillar by pyramidal and basal slip. These mechanisms were accompanied by a strong strain hardening.

Size effects for micropillars of $5 \times 5 \mu\text{m}^2$ to $7 \times 7 \mu\text{m}^2$ were negligible and the critical resolved shear stresses for twin nucleation and growth could be obtained from the applied stress and the Schmid factors. The critical resolved shear for twin nucleation was higher than that for twin growth, and both increased by the same amount with the Al content. Nevertheless, the increase was small (≈ 10 MPa) for 4 at.%Al and large (up to 60-70 MPa) for 9 at.%Al. The solute strengthening in the dilute regime (< 5 at.%Al) was in agreement with the predictions of Labusch-type models based on first principles calculations. However, this approach underestimated the strengthening for large solute contents. In addition, it is shown that Al atoms are more effective in increasing the critical resolved shear stresses for twin nucleation and growth than for basal slip.

Compression tests in micropillars oriented along $[0001]$ showed that the strain hardening in the twinned micropillars was linked to the activation of pyramidal slip. It was found that the critical shear stress for pyramidal slip increased rapidly with the Al content from 98 MPa in pure Mg to 250 MPa in Mg-9 at.%Al. Thus, the information

6.5 Conclusions

about the critical resolved shear stress for twinning and pyramidal slip in Mg-Al obtained in this investigation, together with the corresponding results for basal slip in [191] show that the plastic anisotropy of Mg alloys increases with the Al content.

6.5 Conclusions

CHAPTER 7

Conclusions and future work

7.1 Conclusions

The main conclusions of the work carried out in this doctoral thesis are the following:

- Based on the experimental diffusion data available in the literature for the Mg-Al, Mg-Zn and Mg-Al-Zn systems, the atomic mobility of Al, Zn and Mg in hcp Mg-Al-Zn ternary alloys has been assessed via the Parrot Model of DICTRA software package in conjunction with the corresponding thermodynamic database. The optimized set of atomic mobility parameters could successfully predict the composition profile and the diffusion paths in binary and ternary diffusion couple experiments.

7.1 Conclusions

- A high-throughput approach has been developed to determine the diffusion and mechanical properties of anisotropic hcp metallic alloys and it has been demonstrated to the hcp Mg-Al system. The novel approach has been developed by characterizing the diffusion couple techniques with advanced microstructural (electron probe microanalysis, electron backscatter diffraction) and micromechanical (micropillar compression) characterization techniques.
- The anisotropic interdiffusion coefficients of Al in hcp Mg were extracted at 673 K and 723 K as a function of the grain orientation and Al content using the high-throughput technique. The leakage of grain boundaries in the polycrystalline diffusion couple was found to be negligible when the grain boundaries were perpendicular to the scanning route of the composition profiles. An explicit comprehensive expression of the interdiffusion coefficients as a function of Al content, grain orientation and temperature was derived.
- The effect of Al content on the deformation by basal slip in Mg alloys was analysed by means of micropillar compression tests in grain suitably oriented for basal slip in the diffusion couple. The influence of the Al content and temperature on the deformation mechanisms and on the “smaller is stronger” size effect was determined. Based on this analysis, it was possible to estimate the contribution of the Al solute atoms to the critical resolved shear stress for basal slip at 373 K. The experimental data followed the Labusch model for solid solution hardening and were in good agreement with previous experimental data obtained by bulk compression of single crystals.
- The effect of Al content on the deformation by twin nucleation and growth as well as by pyramidal slip in Mg alloys was analysed by means of micropillar

compression tests in grains suitably oriented for twining or pyramidal slip, respectively, in the diffusion couple. The deformation mechanisms were observed to be independent of the micropillar dimensions and Al content. The stress for twin nucleation was identified by a sudden strain burst due to the nucleation of one or two twin variants in the upper region of the micropillar. Afterwards, twin propagation occurred at a constant stress until the whole micropillar was twinned and deformation was partially accommodated by deformation of the twinned micropillar by pyramidal and basal slip. Based on these results, the influence of the Al content on critical resolved shear for twin nucleation and growth as well as for pyramidal slip was determined. The solute strengthening for twin growth in the dilute regime (< 5 at.%Al) was in agreement with the predictions of Labusch-type models supplemented with first principles calculations, however, this approach was found to underestimate the strengthening for large solute contents. The results for the critical resolved shear stress for basal and pyramidal slip and twinning obtained in this investigation showed that the plastic anisotropy of Mg alloys increases with the Al content.

7.2 Future work

A new high-throughput methodology has been developed in this doctoral thesis to assess the diffusion and mechanical properties of anisotropic hcp metallic alloys. The methodology has been demonstrated with the Mg-Al system, and has the potential to extend to other alloys and to more complex systems. In particular, the following research lines are expected:

- Determine the anisotropic diffusion coefficients in Mg ternary alloys. By

7.2 Future work

designing and fabricating the proper pairs diffusion couples of ternary system (Mg-Al-X or Mg-X-Y), the same methodology is applicable to extracting the diffusion coefficients as a function of solute content and grain orientation in ternary or higher order systems. Such novel information is requisite to any diffusion model for providing realistic anisotropic diffusion in ternary Mg alloys.

- The high throughput strategy could also be extended to investigate the effect of solute content on the critical resolved shear stress for different slip systems and twinning for ternary alloys. And it is particularly helpful to analyze the synergy between different type of solutes and elucidate other strengthening mechanisms, including precipitation hardening. Moreover, it could also be extended a wider temperature range.

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