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**High-throughput screening of strength and creep
properties in Mg-Zn alloys**

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Abstract

Magnesium has attracted significant attention due to its lowest density among the structural metallic alloys and its potential to solve severe global environment issues, not only in transport, but also in electronics and medical applications. However, some drawbacks limit its widespread application, like its low ductility and formability, resulting from its high mechanical anisotropy and the large difference in critical resolved shear stress (CRSS) between the soft (basal slip and extension twinning) and the hard (prismatic and pyramidal slip) deformation modes. Some of these limitations might be overcome by chemical alloying and suitable thermal treatments that have the potential to balance the CRSS between the soft and hard deformation modes. However, conventional alloy design is costly and time consuming, because it relies on processing a large number of alloys and testing them mechanically using conventional methods. In addition, it is often difficult to extract the effect of alloying elements on individual deformation modes using these conventional methods, because the mechanical behaviour is strongly influenced by other factors like texture or grain size. In this work, a novel high-throughput methodology is proposed, based on the combination of diffusion couple and advanced nanomechanical testing methods, to directly measure the effect of alloying on the CRSS of individual deformation modes in Mg alloys.

The methodology was tested on Mg-Zn alloys. Preliminary studies using nanoindentation revealed that this technique can provide qualitative trends on the strengthening effect of Zn and the rate controlling deformation mechanisms as a function of Zn content and temperature. However, the technique was unable to provide quantitative estimates of the CRSS of individual deformation modes. On the contrary, micropillar compression tests in selected orientations were much more suitable to isolate individual deformation modes. This way, a complete assessment of the effect of Zn content and temperature on the CRSS for basal slip, extension twinning, and prismatic slip was performed in Mg-Zn alloys, up to Zn contents of 2 at.%. This range covered both diluted and supersaturated Mg-Zn alloys. The study was performed in three different metallurgical conditions to assess the effect of Zn distribution on the strength of the deformation modes: as-quenched, for which the Zn solute atoms remain homogeneously

dispersed in solid solution; room-aged, for which the Zn atoms tend to form small Zn rich clusters; and peak-aged, for which the Zn atoms form rod-shape β_1' (MgZn_2) precipitates.

It was found that, in the solid solution regime, the Zn atoms induce basal slip and extension twinning strengthening and softening of prismatic slip. The strengthening effect for basal slip was moderate, but much larger than what can be expected for diluted alloys, and this was related to short range order effects. The strengthening for twinning was significantly larger than for basal slip, and the mechanism responsible was found to be preferential Zn segregation to the twin boundaries. Finally, the softening of prismatic slip was found to contribute to the activation of cross-slip between basal and prismatic planes.

With respect to aged conditions, it was found that the strengthening of basal slip and extension twinning provided by the β_1' (MgZn_2) precipitates is much larger than that found for the solid solution condition with the same Zn content. The precipitates were shearable by the basal dislocations and order strengthening was the mechanism responsible for the hardening. It was found that the β_1' (MgZn_2) precipitates induce a strong pinning effect on twin boundary migration, but the strengthening of extension twinning was slightly lower than for basal slip.

The results demonstrate that Zn alloying in both the solid solution and aged conditions, contribute to a reduction in the plastic anisotropy of Mg. Overall, the methodology was successful not only for screening purposes, but also to answer fundamental questions on the mechanisms of interaction of the solute atoms with the different deformation modes. Therefore, the novel high throughput experimental methodology can be readily applied to other Mg alloys.

Resumen

El Magnesio ha atraído un interés significativo debido a que posee la menor densidad entre los materiales metálicos estructurales. Por lo tanto, presenta un alto potencial para aliviar algunos de los problemas medioambientales a los que nos enfrentamos, no solo en aplicaciones de transporte, sino también en electrónica y en aplicaciones biomédicas. Sin embargo, presenta algunas desventajas que limitan su uso extendido, como su baja ductilidad y formabilidad, que resultan de su alta anisotropía mecánica y la elevada diferencia en la tensión resuelta crítica de deslizamiento (CRSS, del inglés) entre los modos blandos (deslizamiento basal y maclado por extensión) y duros (deslizamiento prismático y piramidal) de deformación. La aleación química y los tratamientos térmicos pueden ayudar a superar estas limitaciones, ya que tienen el potencial de equilibrar las CRSS de los modos blandos y duros. Sin embargo, el diseño convencional de aleaciones es costoso y largo, ya que implica el procesamiento y el ensayo mecánico de un elevado número de aleaciones. Además, en general, es difícil cuantificar el efecto de los elementos de aleación en cada uno de los modos de deformación, ya que el comportamiento mecánico es fuertemente influido por otros factores como la textura y el tamaño de grano. Este trabajo propone un método novedoso de alto rendimiento basado en la combinación de pares de difusión con ensayos nanomecánicos avanzados, para medir directamente el efecto de los elementos de aleación en la CRSS de modos individuales de deformación en aleaciones de Mg.

La metodología se ensayó en aleaciones de Mg-Zn. Los estudios preliminares basados en nanoindentación revelaron que esta técnica puede proporcionar tendencias cualitativas acerca del efecto endurecedor del Zn y los mecanismos que controlan la tasa de deformación en función del contenido de Zn y la temperatura. Sin embargo, la técnica no fue capaz de proporcionar medidas cuantitativas de las CRSS de modos individuales de deformación. Al contrario, se determinó que la técnica de compresión de micropilares en orientaciones específicas es mucho más adecuada para aislar modos individuales de deformación. De esta manera, se llevó a cabo una evaluación completa del efecto del contenido de Zn y la temperatura en las CRSS para deslizamiento basal, maclado por extensión y deslizamiento prismático, para contenidos de Zn hasta el 2 % at. Este rango

cubre tanto aleaciones de Mg-Zn diluidas como supersaturadas. El estudio se llevó a cabo en tres estados metalúrgicos distintos: tras temple, en el cual los átomos de Zn permanecen homogéneamente distribuidos en solución sólida; tras envejecimiento natural, en el que los átomos de Zn tienden a formar cúmulos ricos en Zn de pequeño tamaño; y tras envejecimiento artificial, en el que los átomos de Zn dan lugar a la formación de precipitados de β_1' (MgZn_2) de forma cilíndrica.

Se encontró que, en la condición de solución sólida, los átomos de Zn inducen el endurecimiento del deslizamiento basal y el maclado por extensión, y el ablandamiento del deslizamiento prismático. El efecto endurecedor de los sistemas basales es moderado, pero mucho mayor que el esperado para aleaciones diluidas, debido a efectos de orden de corto alcance. El efecto endurecedor sobre el maclado por extensión es mucho más acusado que para el deslizamiento basal, y se determinó que el mecanismo responsable es la segregación preferencial de los átomos de Zn en la fronteras de macla. Por último, se determinó que el ablandamiento de los sistemas prismáticos contribuye a la activación del deslizamiento cruzado entre sistemas basales y prismáticos.

En el caso de la condición envejecida artificialmente, se encontró que el endurecimiento de los sistemas basales y el maclado por extensión producido por los precipitados de β_1' (MgZn_2) es mucho mayor que en el caso de la condición de solución sólida, para el mismo contenido de Zn. Se determinó que los precipitados eran cortados por las dislocaciones basales y que el mecanismo responsable era el endurecimiento por ordenamiento. También se constató que los precipitados de β_1' (MgZn_2) inducen un fuerte anclado de las fronteras de macla, y como resultado, el grado de endurecimiento del maclado es ligeramente superior al de los sistemas basales.

Los resultados demuestran que la aleación con Zn reduce la anisotropía mecánica del Mg, tanto en condición de solución sólida como envejecida. En definitiva, se demuestra el éxito de la metodología, no sólo para el cribado de aleaciones de Mg, sino también para responder a cuestiones fundamentales acerca de los mecanismos de interacción de los elementos de aleación con los modos de deformación. Por lo tanto, la metodología de alto rendimiento propuesta tiene un alto potencial para ser aplicada en otras aleaciones de Mg.

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List of acronyms

Al	Aluminum
AM40	4 wt.% Al, 0.4 wt.% Mn, Mg balance
AM60	6 wt.% Al, 0.4 wt.% Mn, Mg balance
APB	Anti-phase boundary
APT	Atom probe tomography
AQ	As-quenched
AZ31	3 wt.% Al, 1 wt.% Zn , Mg balance
AZ91	9 wt.% Al, 1 wt.% Zn , Mg balance
BSE	Backscattered electrons
BF	Bright-field
Ce	Cerium
CRSS	Critical resolved shear stress
Dy	Dysprosium
D	Diffusion coefficients
DP	Diffraction patterns
DF	Dark field
EPMA	Electron probe micro-analyzer
EBSD	Electron backscatter diffraction
EBSP	Electron backscatter diffraction patterns
EDS	X-Ray energy dispersive spectroscopy
FCC	Face cubic crystal
Fe	Iron
FIB	Focused ion beam
GB	Grain boundary
Gd	Gadolinium
G.P zone	Guinier–Preston zone
HCP	Hexagonal close-packed
HAADF	High angle annular dark-field imaging
HT	High temperature

List of acronyms

La	Lanthanum
Mg	Magnesium
Mn	Manganese
Nd	Neodymium
NanoDMA	Nanoscale Dynamic Mechanical Analysis
OM	Optical microscopy
PA	Peak aged
Q	Activation energy
RA	Room temperature aging
RE	Rare earth elements
RT	Room temperature
SAD	Selected area diffraction
SAED	Selected Area Electron Diffraction
SE	Secondary electrons
SEM	Scanning electron microscopy
SRS	Strain rate sensitivity
SF	Schmidt factors
SRO	Short range order
SFE	Stacking fault energy
STEM	Scanning transmission electron microscope
TBS	Twin boundaries
TD	Twin dislocation
TEM	Transmission electron microscopy
TKD	Transmission Kikuchi Diffraction
TT	Tension twinning
Ti	Titanium
V*	Activation volume
WE43	3.7~4.3wt.%Y, 2.4~4.4 wt.%, Rare earths, 0.4 Zr, Mg balance
Y	Yttrium
Zn	Zinc
Zr	Zirconium

Chapter 1 Introduction

1.1 Magnesium and its alloys

Magnesium (Mg), as the lightest (1.74 g/cm^3) structural metal currently available on earth, is a promising candidate for various transport applications, such as automobiles. Mg [1] is a naturally abundant element, following iron, oxygen and silicon and was first purified by Sir Humphrey Davy in 1808, by electrolyzing a mixture of magnesia (magnesium oxide, MgO) and mercuric oxide (HgO). Table 1.1 compares selected physical properties of Mg, Ti, Al and steel.

Table 1.1: The comparison of the physical properties of Mg with other structural materials.

Alloy	Specific gravity (g/cm^3)	Melting point ($^{\circ}\text{C}$)	Young's Modulus (GPa)	Shear modulus (GPa)	Yielding stress (MPa)	Elong. (%)
Mg	1.74	650	45	17	98	5
Al	2.74	660	70	26	88	45
Ti	4.5	1650	116	44	500	15
Steel	7.86	1535	211	82	265	45

The main advantages of Mg are:

1) Excellent specific strength with a strength-to-weight ratio of about $158 \text{ kN}\cdot\text{m/kg}$, which makes it an excellent candidate for weight reduction applications, in particular in the transport industry [2]. With respect to automotive applications, Mg alloys are applicable for parts with less structural responsibility, such as gearbox housings or steering wheels, seat frames, driver's airbag housings or steering column housings. Some examples of aircraft parts made of Mg alloys are cockpit instrument panel, service door inner and panel rudder pedal (Fig. 1.1).

2). Mg alloys are bio-absorbable and thus suitable for biomedical implants. This feature is very interesting for absorbable implants as it removes the need of a second surgery to remove the implant. Absorbable metal stents, which are currently made of Mg, are a good example of this application.

1.1 Magnesium and its alloys

Fig. 1.1: Examples of industrial components made of Mg alloys [3].

However, Mg and its alloys have some drawbacks restricting their suitability for application as structural materials, such as low strength, low ductility and high mechanical anisotropy at RT, poor behaviour at high temperatures, high percentage of shrinkage cracks during solidification, high chemical reactivity and low corrosion resistance. One strategy to overcome these limitations is chemical alloying with elements that form precipitates and intermetallic compounds, which can modify the deformation mechanisms and microstructure of Mg alloys. The most common alloying elements used in Mg alloys and their properties are summarized in Fig. 1.2 [2,4–8]:

- Al is the most commonly-used alloying element in Mg alloys, which improves castability with reduced micro-porosity, while increasing hardness and strength by solid solution and precipitation hardening [5].
- Zn is usually added together with Al, leads to increase the strength without ductility loss. In addition, it increases fluidity of the melt [6].
- Li reduces the density and improves the ductility by changing the crystal structure to body centred cubic (BCC), when the Li content is higher than 5wt.% [7].
- Mn improves the resistance of Mg-Al and Mg-Al-Zn alloys against salt-water corrosion. However, its effectiveness is limited by the low solubility of Mn in Mg [8].
- Rare metals, such as Nd, Ce, La and Y, increase the strength (specially at high temperatures) and the creep and corrosion resistance. In addition, some alloying elements have been proven to decrease the difference in strength between basal and non-basal slip systems, contributing to a reduced mechanical anisotropy.

1.2 High throughput screening methodology

- Ca contributes to grain refinement, enhancing the creep resistance and reducing corrosion rates [6].
- Zr is an excellent grain refiner when incorporated into Mg alloys.

Fig. 1.2: Schematic diagram showing the trends and the significant research directions in Mg alloy development.

1.2 High throughput screening methodology

Classical strategies used to design new advanced metallic alloys for structural applications [9,10] include defining the chemical composition, optimizing the thermo-mechanical treatments, manufacturing the alloys and testing them using conventional methods. The thermo-mechanical history is essential to modify the distribution of the solute atoms and the final microstructure, such as the size and shape of the grains, their texture and the spatial distribution and size and shape of the second phases precipitates. Correspondingly, the final properties (mechanical, magnetic, electrical, etc.) can exhibit dramatic variations as a function of chemical composition and thermo-mechanical history. However, this approach is usually implemented following a ‘trial-and-error’ path which is expensive and time consuming and demands significant amounts of materials. It is, therefore, urgent to develop new fast and cost-effective experimental methodologies to accelerate the discovery of new materials.

High throughput screening techniques, also called combinatorial methodologies, were initially applied in the pharmaceutical industry [11]. They have the potential to become a promising and powerful new paradigm for the screening of new materials and the generation of large datasets of material properties that can be coupled with simulation

1.2 High throughput screening methodology

predictions [12]. The proposed methodology is shown in Fig. 1.3 and involves the fabrication of specimens where the material parameters of interest (typically composition) vary within a wide range coupled with efficient characterization approaches of the local microstructures and properties [9]. The diffusion multiple approach could provide specimens with a wide range of chemical composition variations. Its combination with newly developed high resolution characterization and testing techniques at the micrometer scale provides the potential to perform localized measurements as a function of composition and phase in a much more effective and systematic way than using individual alloyed samples.

Fig. 1.3: Graphic summary of the diffusion multiple approach for the high throughput material research [10].

Diffusion multiples were initially utilized to construct thermodynamic (phase diagram) [10] and kinetic (diffusivities) [13] databases in multicomponent alloys, by combining local characterization techniques, such as electron probe micro-analysis (EPMA) and electron backscattered diffraction (EBSD), for the determination of local chemical composition and phase identification, respectively. More recently, microscale thermal conductivity probing and other microscale property measurement tools [14] have allowed, not only mapping functional properties (such as thermal, magnetic or optical properties), but also providing insights into fundamental questions regarding order-disorder transformations, site preference of intermetallic compounds and point defect density variations, as a function of composition [9,15]. However, the use of diffusion multiples to screen mechanical properties remains elusive, due to the difficulties associated with measuring mechanical properties at small scales [10]. If these difficulties

are overcome, the approach would provide a very valuable tool for screening new alloys and for gaining fundamental knowledge on the effect of solute atoms and precipitates in mechanical behaviour [15].

1.3 Objectives and structure of the thesis

In this context, the main objective of this work was to evaluate the potential of combining the diffusion couple approach with novel advanced nanomechanical testing methods, to directly measure the effect of alloying on the CRSS of individual deformation modes in Mg alloys. For validation purposes, the work was focused on the well-known Mg-Zn alloying system as a function of metallurgical condition. The objective was to assess, not only the effect of composition, but also the effect of the distribution of the Zn atoms in the form of homogeneous solid solutions, clustered solid solutions and precipitated alloys.

The structure of the thesis is organized as follows. After a literature review on Mg alloys in chapter 2 and a description of the experimental techniques used in chapter 3, chapter 4 describes the preliminary studies performed using nanoindentation to measure the mechanical properties as a function of Zn content. Since nanoindentation was unable to provide quantitative measurements of the effect of Zn content on the different deformation modes present in Mg alloys, the rest of the thesis focuses on the use of micropillar compression. Chapter 5 summarizes the effect of Zn alloying in basal slip, while chapter 6 focuses on its effect on extension twinning and chapter 7 on prismatic slip. Finally, the most important conclusions and proposals for future work are summarized in chapter 8.

Chapter 2 Literature review

2.1 The crystal structure of magnesium

The crystal structure of magnesium is hexagonal closed packed (HCP) at RT with the ABABAB layers stacking sequence as shown in Fig. 2.1. There are six atoms in the HCP unit cell: 12 atoms in the corners of the hexagonal top and bottom layers that contribute with 1/6 atom to the unit cell; 2 atoms in the centre of these hexagons, that contribute with 1/2 atom and 3 atoms in the mid-layer that are completely contained within the unit cell. If r is the atomic radius, the lattice parameters are: $a_1 = a_2 = a_3 = 2r$, lying on the basal plane, and $c = 4\sqrt{2/3}r$, which is perpendicular to the basal plane. The c/a ratio of the Mg HCP lattice is 1.623 ($a=0.32092$ nm and $c=0.52105$ nm) which is close to the theoretical value of 1.633 for the ideal HCP structure [16].

Fig. 2.1: *The Mg-HCP unit cell*

The Miller-Bravais indices used to index lattice planes and directions in the HCP structure use a four-index notation, based on the lattice vectors a_1 , a_2 , a_3 and c . Considering that $a_3 = -(a_1 + a_2)$, lattice vectors are expressed as $d = ua_1 + va_2 + ta_3 + wc$, where $u + v = -t$. The Miller indices for lattice planes can be derived by taking the reciprocal of the intercepts of the planes on the respective axis. These values are then reduced to the smallest integers, having the same ratio. The closed packed plane in the HCP direction is the basal plane, (0001), with the most closed packed directions belonging to the family $\langle 2\bar{1}\bar{1}0 \rangle$.

2.2 Plastic deformation mechanisms

2.2 Plastic deformation mechanisms

The most important deformation mechanisms in crystalline materials rely on dislocation motion and twinning [17]. In general, the two mechanisms of dislocation motion include dislocation slip or glide, in which motion occurs on the slip plane formed by the dislocation line and the Burgers vector and dislocation climb, which occurs when the dislocation moves out of the slip plane, usually by thermal activation.

2.2.1. Dislocation glide

The onset of dislocation glide occurs when the projection of the applied stress on the slip plane along the slip direction reaches a critical value, called the critical resolved shear stresses (CRSS). This phenomenon provides the yield criterion for single crystals, which depends on the relative orientation of the applied force with respect to the active slip plane and slip direction, following Schmid's law. Consider the single crystal depicted in Fig. 2.2 which is being deformed in tension by an applied force F along the vertical axis, which corresponds to a tensile stress, $\sigma = \frac{F}{A}$, where A is the cross-sectional area.

Fig. 2.2: Determination of the resolved shear stress by the schematic representation of the relation between the applied force F and the resolved stress τ . ϕ is the angle between the tensile axis and the vector normal to the slip plane and λ is the angle between the tensile axis and the vector in the slip direction [18].

The force has a component $F \cos \lambda$ in the slip direction, where λ is the angle between F and the slip direction. This force acts over the slip plane, with an area $A / \cos \phi$, where

ϕ is the angle between F and the normal to the slip plane. Thus, the shear stress τ , resolved on the slip plane and in the slip direction, is given by $\tau = \frac{F}{A} \cos\phi \cos\lambda$.

In general, the CRSS required to activate dislocation slip is minimum in the planes with the highest packing density and along the direction with the shortest Burgers vector. In the case of Mg, this corresponds to the glide of $\langle a \rangle$ basal dislocations on the basal slip plane. Since only two slip systems of this type exist in Mg, other slip systems can be activated depending on loading orientation. Besides basal slip, other common slip systems in Mg include $\langle a \rangle$ prismatic slip, $\langle a \rangle$ pyramidal I slip and $\langle c+a \rangle$ pyramidal II slip, as shown in Fig. 2.3.

Fig. 2.3: *Principal slip and twinning systems in Mg.*

2.2.2. Twinning

Twinning is another important plastic deformation mechanism in Mg. Deformation twinning is a homogenous shear process and results in the reorientation of the original atomic lattice (parent) to the product crystal (twin) with mirror symmetry [19,20]. The mirror plane is the twin plane as shown in Fig. 2.4. The open circles represent the position of atoms before twinning and the black circles the positions after twinning. The atoms above x-y are mirror images of the atom composition plane below and therefore x-y represents the trace of the twin plane. The description of twinning in crystalline lattices follows the formal notation ($K1, \eta1, K2$ and $\eta2$) [21]. There are two planes $K1$ and $K2$ that remain undistorted during twinning. $K1$ is the first undistorted plane, which is also the twinning plane and $K2$ is the second undistorted plane. $\eta1$ is the direction of the twinning shear corresponding to $K1$ and $\eta2$ is the second characteristic direction. This second direction lies in the $K2$ plane. The plane of shear contains $\eta1, \eta2$, and is normal to the planes $K1$ and $K2$.

Fig. 2.4: A twinning shear event. Twinning parameter formal notation (K_1 , η_1 , K_2 and η_2).

The most common types of twinning in Mg include tension and compression twins. It has been commonly found that when loading Mg crystal along the $\langle c \rangle$ axis, $\{10\bar{1}1\} \langle 10\bar{1}2 \rangle$ twins form under compression and $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$ twins form under tension, as shown in Fig. 2.3. Hence, they are referred to as compression twins and tension or extension twins, respectively. The development of a twin is a complex process which involves two steps: nucleation and growth [20,22]. While the CRSS required for the propagation or growth of an existing twin is moderately small, the nucleation of a twin embryo is a volume activation process that requires quite severe stress states [23–28]

2.2.3. Anisotropic mechanical behaviour of Mg

The mechanical behaviour of Mg is strongly anisotropic, which is not surprising considering the large number of deformation modes potentially present. Dislocation slip in HCP Mg crystals mainly occurs by basal and prismatic slip along $\langle a \rangle$ directions as well as by $\langle c+a \rangle$ dislocations on the second-order pyramidal planes. First order pyramidal slip along $\langle a \rangle$ directions is not usually observed, and in any case, it can be considered geometrically equivalent to the combined action of $\langle a \rangle$ dislocations on basal and prismatic systems through cross-slip. The critical resolved shear stress (CRSS) for dislocation slip in the basal $\{0001\} \langle 11\bar{2}0 \rangle$ system is very low (~ 0.5 MPa [29–31]) as compared with the CRSS values (40 MPa) for both $\{01\bar{1}0\} \langle 11\bar{2}0 \rangle$ prismatic and $\{11\bar{2}2\} \langle \bar{1}1\bar{2}3 \rangle$ pyramidal slip in pure Mg [32–34]). Those slip systems provide enough independent slip systems to accommodate an arbitrary plastic deformation according to the Taylor's criterion [35]. However, since pyramidal slip is hard to activate, tensile twinning tends to accommodate strain along the $\langle c \rangle$ axis, because the CRSS for twinning (7–12 MPa) in pure Mg is much lower [18,24,31,112,176,192].

2.3 Creep deformation of magnesium

The current interest in the creep behaviour of magnesium alloys arises from the expected economic and environmental benefits particularly in the automobile's power-train applications, requiring creep resistance at temperatures up to 200 ° C. Due to the low melting temperature of magnesium and its hexagonal crystal structure (HCP) that allows relatively rapid diffusion rates, creep becomes a dominant design criterion, especially for applications such as engine blocks and transmission cases.

Creep deformation mechanisms in Mg alloys have been extensively investigated over the past years [36–38], including plasticity (dislocation glide), power law creep (climb plus glide), power law breakdown (glide plus climb), recovery (dislocation climb) and diffusion (volume, grain boundary or dislocation pipe) controlled creep. The steady-state or secondary creep is usually expressed as [39]:

$$\dot{\epsilon} = \frac{ADGb}{kT} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (2.1)$$

where $\dot{\epsilon}$ is the steady-state creep rate, D is the diffusivity (lattice or grain boundary), G is the shear modulus, b is the Burgers vector, k is the Boltzmann constant, T is the temperature in Kelvin, d is the grain size, p is the grain size exponent, σ is the applied stress and n is the creep exponent of the flows stress. For a constant T , $\dot{\epsilon}$ can be well described by the simple expression:

$$\dot{\epsilon} = K \cdot \sigma^n = K \cdot \sigma^{\frac{1}{m}} \quad (2.2)$$

where n is the stress exponent, K is a constant and m is the strain rate sensitivity (SRS), defined as

$$m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}} \sim \frac{\partial \ln H}{\partial \ln \dot{\epsilon}} = \frac{1}{n} \quad (2.3)$$

The m (SRS) is an important parameter that depends on the operating deformation mechanisms and that can have important implications on the overall structural performance. For instance, a reduction in the SRS is known to decrease the ductility.

The activation volume is a physical quantity that gives an indication of the physical volume involved in the rate-controlling deformation processes. It is given by

$$V^* = \frac{2.8 \times \sqrt{3} kT}{H} \left(\frac{\delta \partial \ln \dot{\epsilon}}{\partial \ln H} \right) \quad (2.4)$$

2.3 Creep deformation of magnesium

where k is the Boltzmann constant, T is the absolute temperature (degrees K), m is the strain-rate sensitivity and σ is the yield stress. Table 2.1 lists the typical activation volumes of some common deformation mechanisms.

Table 2.1: Activation volume of common deformation mechanisms [12].

Deformation mechanism	Activation volume (V^*)
Grain boundary diffusion	$1\sim 10b^3$
Dislocation nucleation	$1\sim 10b^3$
Confined layer slip	$10\sim 100b^3$
Cross slip	$10\sim 1000b^3$
Dislocation glide	$100\sim 1000b^3$
Dislocation forest cutting	$>1000b^3$

In pure Mg, the first detailed investigation on the creep of single crystals was conducted on specimens favouring either basal or prismatic slip [30,31]. Alloying is expected to affect the operating deformation mechanisms, and in turn the SRS, but this aspect in Mg alloys has not been examined extensively. Stanford *et al.* investigated the effect of Al and Gd solutes on the SRS of magnesium alloys, showing a reduction of SRS with the alloying content [40]. Hidetaoshi went one step further by determining the effect of alloying elements on the SRS associated with different slip systems in Mg–0.3 at.% X (X = Al, Ca, Li, Y or Zn). The results suggested that alloys containing Al, Y, Ca and Zn have higher activation volume than pure Magnesium, whereas the addition of Li gives a lower activation volume [41]. Some values for m and V^* are summarised in Table 2.2. However, more work is required to elucidate the physical reasons for this.

Table 2.2: Literature data of strain rate sensitivity m and activation volume V^* for different deformation modes in Mg alloys.

Alloy	Deformation mode	m	Activation volume (V^*)
AZ31 [42]	Basal slip	0.01	-
	Prismatic slip	0.0125	-
	Pyramidal slip	0.03	-
	Extension twin	0.0083	-
Pure Mg [43]	Basal slip	~ 0.01	$25.3b^3$
		0.0212	-
Mg-0.3at.%Zn [44]	Cross slip	-	$50.3b^3$
WE43 [45]	Prismatic slip	0.008 ± 0.004	$600b^3$
	Pyramidal slip	0.007	$17b^3$
AM40 [46]	-	0.003	-
AM60	-	0.003	-
AZ91	-	0.0037	-
AZ31 [47]	Diffusional type	0.008	$100b^3$
	Non-diffusional type	0.06	$15b^3$

2.4 Alloying effects on dislocation glide

2.4.1 Solid solution effects

Solid solution effects arise from complicated interactions between mobile dislocations and solutes in the crystal lattice. There are two classical theories for solution strengthening in general: the strong-pinning and the weak-pinning theory.

The strong-pinning theory (Friedel [48], Fleischer [49,50]) only takes the solute atoms in the slip plane into consideration. The strengthening is based on the interaction between the dislocation segment and the solute atom within an $L \times L$ area, neglecting the influence from other nearby solutes. Under stress, the pinned dislocation segment bows out in the area, exerting a counteractive force to the maximum resistive force (F_{max}). The yield stress, σ , of a random alloy at 0 K can be estimated from:

$$\tau_0 = \left(\frac{F_{max}}{2\Gamma} \right)^{\frac{3}{2}} \left(\frac{2\Gamma}{b^2} \right) c^{\frac{1}{2}} \quad (2.5)$$

where Γ is dislocation line tension, c the atomic composition and b the magnitude of Burgers vector.

On the contrary, the weak-pinning theory (Mott-Nabarro [51,52], Labusch [53], Nabarro [54]) includes the effect of additional solute atoms close to the slip plane. Instead of the maximum pinning force from individual atoms, the predominant strengthening factor is the collective elastic interaction between the mobile dislocation and the surrounding solute atoms. In alloys with a random distribution of solutes, there would be as many repulsive as attractive encounters for mobile dislocations on average [55]. The actual strengthening depends on the variation (trade-off in binding energy and line energy of dislocations) in the energy between dislocation and surrounding solutes during dislocation movement. Therefore, this theory attributes the solution strengthening to the statistical fluctuations in the spatial distribution of solutes within random alloys. Labusch [53] first developed a statistical model to estimate the strength of random alloys at 0 K as:

$$\tau_0 = \left(\frac{F_{max}^4 w}{4\Gamma b^7} \right)^{\frac{1}{3}} c^{\frac{2}{3}} \quad (2.6)$$

where w measures the distance from solute atoms to the slip plane within the range of interest.

It is widely accepted that, at 0 K, the strong pinning theory is the operative strengthening mechanism at low solute concentrations ($\sim 10^{-2}$), while the weak pinning

2.4 Alloying effects on dislocation glide

mode dominates the behaviour at higher concentrations [56]. While none of the original two models takes the influence of temperature into consideration, later modifications of the Labusch model were made, in order to include thermal effects [56–62]. Compared to the collective resistive force in the weak pinning model, the pinning force provided by individual solute atoms is much weaker and more sensitive to the thermal fluctuations. Therefore, the strong pinning strengthening drops rapidly as the temperature increases.

Estimating solute hardening in different slip modes is critical in Mg alloys. With regard to the basal slip mode, the influence of different solute atoms (Zn, Cd, Sn, In, Al, Pb, Bi, Y and Dy) on the CRSS values for basal slip has been studied [63–66], both by experiments and simulations, as summarised in Fig. 2.5. Additionally, tensile tests in single crystal Mg-Al and Mg-Zn [64,67] alloys have shown an increase of the CRSS for basal slip of up to 2.5 MPa and 2 MPa with the addition of 1.6 at. % Al and 0.5 at. % Zn, respectively.

Fig. 2.5: Critical resolved shear stress for the basal slip for different Mg alloys at room temperature from simulation [63–66].

In the case of non-basal slip, studies are very scarce due to the difficulty associated with activating non-basal slip in competition with basal slip and extension twinning, that are much softer. Nevertheless, Akhtar *et al.* [67,68] studied solid solution strengthening in single crystals of magnesium containing Zn oriented for prismatic slip. These tests showed that Zn solutes in the range of 0~0.45 at.% decreased the CRSS for prismatic slip, as shown in Fig. 2.6.

Fig. 2.6: CRSS for prismatic slip in Mg-Zn alloys at different temperatures [67].

This is first ever report of solute softening in an alloy system, although more experimental evidence is needed to verify the mechanism of the softening of prismatic slip mode [69]. First principle simulations in Mg-Zn solid solutions with 0.3~0.5 at.% Zn have suggested that Zn alloying increases the CRSS of basal slip more than that of non-basal slip, eventually reducing the difference in CRSS between different slip systems [70], as shown in Fig. 2.7 (a-c). This is consistent with non-basal slip observations in diluted Mg-0.38 at. % Zn alloys. The effect was similar to that found by simulations for Y and Al, which was found to favour the activation of $\langle c + a \rangle$ dislocation, as shown in Fig. 2.7 d and e, respectively [71], in agreement with experimental observations [72,73]. In summary, solid solution strengthening has already shown the potential to balance the CRSS for basal slip and non-basal slip and therefore, enhance the ductility of Mg alloys.

2.4 Alloying effects on dislocation glide

Fig. 2.7: (a-c) Simulated stress-strain curves for Mg-Zn under different loading orientations [70]; Variation of CRSS of different slip systems for (d) Mg-Y and (e) Mg-Al alloys [71], obtained using simulations at 0 K.

2.4.2 Precipitation effects

Precipitation might be another way to improve the strength and ductility of Mg alloys. The mechanisms for precipitation strengthening can be classified depending on whether the precipitates are shear-resistant or are sharable by the dislocations [74,75].

In shear-resistant particles, the increase in the CRSS for dislocation slip is attributed to *Orowan* mechanisms due to the bowing of dislocations by the precipitates. The level of strengthening depends on different factors, such as, precipitate shape, number density and morphology [76–78], as shown in Fig.2.8. J.D.Robson et.al. [76] predicted that precipitates formed on prismatic planes are more effective on strengthening Mg alloys, than those formed on basal planes. For instance, rod-shape β_1' (MgZn_2) precipitates in Mg-Zn alloys and β (Mg_5Gd) precipitates in Mg-Gd-Y alloys, that form on prismatic slip planes, have shown a more effective strengthening effect than plate-shape β_2' (MgZn_2) in Mg-Zn alloys and β ($\text{Mg}_{17}\text{Al}_{12}$) in Mg-Al alloys, that form on the basal planes.

Fig. 2.8: The calculation of the Orowan stress required to bypass basal plates, prismatic plates, and spherical precipitate for (a) basal slip and (b) prismatic slip [76].

For shearable precipitates, the degree of interface coherency between the particle and the matrix plays a major role on the likelihood of a dislocation shearing the particle [75,79]. A variety of dislocation and particle interaction mechanisms might be responsible for the resistance to shearing, such as interfacial or chemical strengthening, coherency strengthening, stacking-fault strengthening, modulus strengthening and order strengthening. In general terms, the strengthening due to shearable precipitates, τ_p , should follow [74]:

$$\tau_p = \left(\frac{F}{2T}\right)^{3/2} \left(\frac{2T}{bd}\right) \quad (2.7)$$

where T is the dislocation line tension, d is the size of the precipitate in the shear plane and F is a measurement of the resistance of the precipitates to dislocation shearing. For instance, assuming that the dominant mechanism is order strengthening due to the creation of an antiphase boundary (APB) upon particle shearing by the dislocations, for the case of rod-like precipitates perpendicular to the slip plane, equation (2.7) becomes [74]:

$$\tau_p = \frac{\gamma_{APB}}{2b} \left(\frac{d}{\left(\frac{0.953}{\sqrt{f}} - 1\right)d} - f \right) \quad (2.8)$$

where γ_{APB} is the energy of the APB and f is the volume fraction of precipitates.

2.5 Alloying effects on twinning

2.5 Alloying effects on twinning

2.5.1 Solid solution effects

The twin nucleation model is based on the dissociation of sessile dislocations into stable twin loops, while propagation is assumed to occur by a layer-by-layer atomic shearing on twin planes and shuffling to reduce the energy barrier [80,81]. Although large efforts have been devoted to suppress twinning through chemical alloying, the solid solution effect on twinning is not well understood [82]. It is most likely that twin nucleation may be altered by alloying via the change either in the twin-boundary energy or in the atomic shuffling mechanisms [80]. The interaction energies of Al and Zn solutes with the twin boundary and twin dislocation (TD) were computed by M.Ghazisaeidi [83], predicting a strengthening by around 10 MPa for AZ31 at room temperature. In Mg-Y alloys, Stanford [84] found that increasing the Y solute concentration resulted in a reduced $\{10\bar{1}2\}$ twinning activity and the appearance of $\{11\bar{2}1\}$ twins. Moreover, Peng Yi *et al.* [85] simulated the effect of Al and Y solute atoms on twin nucleation and growth. Solute softening was predicted at small solute concentrations for both Al (1 at.%) and Y (1 at.%) and hardening at larger concentrations. This was attributed to the fact that the solute atoms in the diluted regime facilitate the nucleation of TD loops, while at higher concentrations they exert a stronger pinning effect that impedes their expansion. Therefore, solute effects on deformation twinning seem to have a two-fold effect [25], facilitating TD loop nucleation and interfering with TD loop expansion.

2.5.2 Precipitation effects

The widely accepted understanding suggests that precipitates do not prevent twin nucleation, but that they might strongly interfere with the process of twin growth [24,75,81,86–88]. For instance, Stanford *et al.* [89] observed a higher density of small twins in age-hardened Mg-Zn alloys than in precipitate-free samples. There is not a widely accepted view on the basic nature of the interaction between twin boundaries (TB) and precipitates [74]. Yet, understanding these effects is a precondition for including them in physically based models. As early as 1965, Clark [78] reported that rod-shaped precipitates are re-orientated in $\{10\bar{1}2\}$ twins of Mg-5Zn alloys and concluded that this is a result of the precipitates being sheared by the twins. Later, Gharghouri *et al.* [90] reported that precipitates in a Mg-7.7 wt.% Al alloy are engulfed by the TB but not

2.5 Alloying effects on twinning

twinned, leading only to a rigid body rotation, as also observed in recent experiments in Mg-6Zn [77], AZ91[91] , Mg-5Zn polycrystals [92] and Mg-5Zn micropillars [75].

Chapter 3

Materials and experimental techniques

3.1 Fabrication of the diffusion couples

Pure Mg and Mg-2.3 at.% Zn were used to fabricate the diffusion couple. The range of Mg-Zn composition was chosen based on the phase diagram (Fig. 3.1), The eutectic temperature is 613 K (340 °C), and the maximum solid solubility of Zn in magnesium is 6.2 wt.% (or 2.4 at. %) at the eutectic temperature [74]. The equilibrium solid solubility of Zn in magnesium decreases substantially with decreasing temperature, and the controlled decomposition of the supersaturated solid solution of Zn in magnesium can produce an age-hardening effect. The accepted aging process as function of the heat treatment history of Mg-Zn alloys is listed in Table 3.1.

Fig. 3.1: The Mg-Zn phase diagram [93].

Table 3.1: The precipitation sequence in Mg-Zn [74].

Temperature /Time	Precipitation sequence
22°C	Zn clusters → G.P zones and prismatic precipitates
200°C	G.P zones → Zn rich clusters → β_1' (rod shape MgZn ₂) → β_2' (plate shape MgZn ₂)→ β (incoherent Mg ₂ Zn ₃)

3.1 Fabrication of the diffusion couples

Fig. 3.2: *The induction furnace VSG 002 DS, PVA Te-Pla for melting the metal alloys.*

The pure Mg and binary Mg-2.3 at.% Zn alloys were produced by casting from Magnesium and Zinc pellets (purity 99.99%). The pure Mg and Zn pellets were melted at 700°C using an induction furnace VSG 002 DS, PVA Te-Pla (Fig. 3.2) under argon atmosphere, followed by casting in a copper steel mould cavity coated with boron nitride. Before preparation of the diffusion couple, the pure Mg and Mg-Zn alloys were homogenized at 400°C for 7 days. After that, the rods were sectioned into discs of diameter 12 mm and thickness 8 mm. The discs were prepared for diffusional bonding by incrementally polishing the surface with 1 μm and 0.25 μm diamond paste. They were bonded by pressing them for 1h at 400 °C under a compression stress of 15 MPa using a Physical Simulator (GLEEBLE 3800, DSI), shown in Fig. 3.3. Subsequently the bonded discs were encapsulated in Pyrex tubes under an argon atmosphere with the aim of preventing oxidation during annealing. The diffusion annealing step was carried out at 400°C for 336 hours in vacuum, in order to obtain a wide diffusion zone, followed by quenching to room temperature (RT).

Fig. 3.3: *Physical Simulator (GLEEBLE 3800, DSI).*

3.2 Characterization of chemical composition and microstructure

Fig. 3.4 shows the microstructure of the diffusion couple between the pure Mg and the Mg-Zn alloy. The interface was well bonded, and the Zn content changed gradually along the inter-diffusion zone, that spanned a few hundred microns.

Fig. 3.4: (a) *Schematic drawing of the diffusional couple and (b) its corresponding concentration profile measured by EPMA and (c) the HR-SEM image of the diffusion couple.*

The microstructure, chemical composition and crystallographic orientation of the grains found in the inter-diffusion region of interest were examined using a combination of complementary techniques, such as, electron probe microanalysis (EPMA), optical microscopy (OM), scanning and transmission electron microscopy (SEM, TEM), and electron backscattered diffraction (EBSD). Surface preparation for OM, EPMA, SEM and EBSD consisted on grinding on successively finer SiC papers with a grit size of 320, 600, 1000 and 2000. After grinding, the sample was polished using a MD-Mol cloth (Struers®) together with 3 μm diamond paste. This was followed by further polishing, making use of a MD-Nap cloth combined with 0.25 μm diamond paste. The polishing procedure was finished using a MD-Chem cloth (Struers®), with a solution of 75 ml of ethylene glycol, 24 ml of distilled water and 1 ml of nitric acid. The solution was poured into a pre-wet MD-Chem cloth (Struers®) and the sample was subsequently carefully

3.2 Characterization of chemical composition and microstructure

rubbed against the cloth during ~ 45 s following circular paths. The optimal etching time depends on the average grain size of the sample, and thus, this parameter must be tuned for each specific case. Great care must be taken to keep the polished cross-section parallel to the bottom surface during grinding and polishing, in order to avoid alignment errors in the subsequent micromechanical characterization, which will be described later in section 3.3.

3.2.1 Analysis of the chemical composition

The chemical composition within the inter diffusion region was measured by EPMA using a JEOL Superprobe JXA 8900 microscope with a voltage of 20 kV and a current of 50 nA. This technique consists on irradiating the sample surface with an electron beam and analysing the characteristic X-rays generated from the bottom part of interaction volume. Several wavelength dispersive X-ray spectrometers are utilized to record the characteristic X-ray signals and commercial software is used to calculate the alloy composition by comparison with the measured characteristic X-ray signal from standard samples. The EPMA technique allows a measurement accuracy of 0.01 % on the solute content.

3.2.2 Microstructural characterization

The microstructure of the Mg/Mg-Zn diffusion couple was systematically characterized by scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). This section introduces details of each characterization technique.

a) Scanning Electron Microscopy

Field emission gun scanning electron microscopy (FEG-SEM) analysis was carried out in a FEI Helios NanoLab 600i dual beam microscope, in order to obtain a more accurate view of the finer details of the microstructure. FEG-SEM images are formed from a multiplicity of emissions that result at the interaction volume between an incident high energy electron beam and the specimen surface (Fig. 3.5).

Fig. 3.5: Sketch of the signals generated on the interaction between the electron beam and the material surface.

Three main signals can be distinguished: secondary electrons (SE), backscattered electrons (BSE) and X-rays. In particular, the BSEs result from elastic scattering with the atoms of the material, mainly deep within the interaction volume and with little energy loss, while secondary electrons (SE) are produced near the surface of the interaction volume as secondary products, commonly with lower energy. As a result, the BSE contrast reveals changes in the local average atomic number, while the SE contrast is indicative of the surface topography. Additionally, other signals such as X-rays are also by-products of the interaction between the incident electron beam and the sample; the latter are utilized to analyse the local composition, through energy dispersive spectroscopy (EDS).

b) Electron backscatter diffraction

Electron backscatter diffraction (EBSD) has made an impressive impact on the characterization of materials by directly linking microstructure and crystallographic texture. It provides very rich and quantitative datasets, which, in many instances, have forced us to rethink how microstructure should be defined and analysed. Fig. 3.6a is a schematic illustrating the fundamentals of this method. A sample with a flat and highly polished surface and a large tilt angle (away from normal incidence of the electron beam on the specimen surface), of the order of 70° , is required to maximize the intensity of backscattered electrons.

Fig. 3.6: (a) Schematic drawing of an EBSD system; (b) typical EBSD pattern of Si [94].

A sensitive camera that includes a phosphor sensor is used to collect the diffraction patterns inside a scanning electron microscope. The intersection of these cones with the flat phosphor screen of the detector forms regions of enhanced intensity, so-called bands, that constitute Kikuchi patterns (or electron backscatter diffraction patterns, EBSPs), depicted in Fig. 3.6b. These patterns are a gnomonic projection of the diffracted cones, making the band edges appear hyperbolic. The centre lines of the Kikuchi bands correspond to where the diffracted planes intersect with the phosphor screen. Each Kikuchi band can thus be assigned to a diffracting plane, and their intersections correspond to zone axes. From the EBSP, the crystal orientation is identified by a specialized computer software. In this work, EBSD analysis was carried out in the Helios Nano Lab 600i FEGSEM equipped with an HKL Nordlys Nano electron backscatter detector and the Aztec data acquisition and analysis software package. EBSD measurements were conducted at an accelerating voltage of 15 kV and 2.7 nA.

c) Transmission Electron Microscopy

TEM is a very useful technique for the study of defects [19,95], such as dislocations, interfaces, grain boundaries, at very high resolution. In the TEM, the incident electrons, also called primary electrons, emitted from the electron gun are accelerated towards the specimen at energies between 100 and 400 keV. A set of condenser lenses and apertures ensures parallel illumination of the specimen. Upon interaction with the specimen, the primary beam splits between the direct beam, formed by electrons that undergo inelastic scattering without changing the incident direction, and diffracted beams that change their direction through elastic scattering by the lattice planes of the specimen that fulfil the Bragg condition. Depending on the operation of the objective and projection lenses and the set of objective apertures selected, different types of images can be generated. Diffraction patterns (DP) provide crystallographic information such as crystal orientation,

3.2 Characterization of chemical composition and microstructure

lattice parameters, etc., while bright-field (BF) and dark-field (DF) images, generated by selecting either the direct or one of the diffracted beams, hold information about morphology, grain size and defect structure. Finally, phase contrast analysis by combining the direct and diffracted beams allows the generation of high-resolution electron microscopy (HREM) images that can be used to infer information about the crystalline lattice at atomic resolution.

In this work, the examination of very fine microstructural features such as nanoscale precipitates and dislocation arrays was carried out by TEM in a Talos F200X microscope operated at 200 kV. Selected area diffraction (SAD) patterns were utilized to select dark field imaging conditions of specific precipitates. The appropriate reciprocal lattice vector was chosen for dislocation imaging.

d) Atom Probe Tomography

Atom probe tomography (APT) is a nanoscale characterization technique that gives a three-dimensional (3D) image of the position and the chemical nature of each atom inside a material [96]. The interest of the technique is based on the ability to provide a global and a local view of the content of the material at the atomic scale (around 0.1-0.3 nm resolution in depth and 0.3-0.5 nm laterally). The global view of the chemical distribution of atoms is useful to define different phases included in the material, whereas the local view gives the ability to quantify the number of atoms included in each specific phase with a resolution close to angstroms.

Fig. 3.7 shows the most important parts of the APT instrument. The sample is prepared as a short tip with a radius of curvature of about 50 nm, placed in a vacuum chamber at cryogenic temperature. Atoms are field evaporated (in the form of ions) from the specimen surface and their trajectory is intercepted by a position-sensitive detection system placed in front of the specimen. This detector must have high timing measurement abilities. The chemical nature of each detected atom is defined by time-of-flight mass spectrometry and the original 3D position of each atom inside the material is calculated from the position information measured by the detection system and the geometrical properties of APT.

3.2 Characterization of chemical composition and microstructure

Fig. 3.7: The CAMECA LEAP4000XHR APT system [97].

Fig. 3.8: Schematic drawing of the atom probe technique (APT) and schematic arrangement of a 3D atom probe. Atoms at the surface of the specimen are evaporated by field effect and fly toward a detection system, which determines XY positions and the chemical nature of each atom.

3.2.3 Focused ion beam milling

Microstructural characterization and the nano-mechanical testing methods (like micropillar compression) employed in this work rely on the accurate fabrication of small volume specimens with specific geometries, which can be implemented by FIB milling. The basic concept of a focused ion beam (FIB) microscope is similar to that of the scanning electron microscope, but the former uses ions like Gallium (Ga^+), Helium, etc., instead of electrons, for imaging or removal of material.

Almost all materials can be structured by FIB, ranging from soft matter (polymers) to ultra-hard materials (diamond). However, when using FIB for surface structuring, it should be kept in mind that this method can lead to ion implantation, thermal stresses and defect formation. Most FIB microscopes are equipped with an additional scanning electron column. Such SEM/FIB systems are extremely useful since they allow for *in situ* observation with the electron beam during ion beam milling. Another advantage of the SEM/FIB systems is that they can also be used for ion-beam assisted deposition in

3.2 Characterization of chemical composition and microstructure

selected locations. This is very useful when depositing metals (like Pt) to protect selected locations from further interaction with the ion beam as shown in Fig. 3.10. The FIB/SEM system employed in this work was a FEI Helios NanoLab™ DualBeam™ 600i FIB microscope, as shown in Fig. 3.9. The ion beam is aligned at 52° with respect to the electron beam, therefore the ion beam impinges at 90° with respect to the sample while electron imaging takes place at 52° , as shown in Fig. 3.9.

Fig. 3.9: (a) FEI Helios Nano-Lab dual-beam FIB-FEGSEM used in this work; (b) schematic diagram of the components of the microscope [165].

Fig. 3.10: Schematic diagram of an ion beam induced platinum deposition process [166].

a) TEM lamella fabrication

Lamellae for TEM examination were prepared by a trenching-and-lift-out procedure consisting on the following steps illustrated in Fig 3.11: a) selection of the area of interest and deposition of a Pt protective layer to avoid implantation of Ga^+ ions; b) rough milling

3.2 Characterization of chemical composition and microstructure

of trenches to remove the surrounding material, thus carving a lamella of 1~1.5 μm in thickness; c) thinning of the lamella with low ion beam currents to decrease the implantation damage; d) performance of bottom and lateral cuts, leaving the lamella attached to the bulk by just one side; e) welding of the lamella.

Fig 3.11: TEM lamella preparation process using focus ion beam technique [166]: (a) Pt deposition, followed by (b-e) lamella separation from the bulk; (f) lift-out of the lamella; (g-h) Pt welding of the lamella to the TEM grid; (i) final thinning (~ 100 nm thickness). (adapted from <https://www.pdx.edu/cemn/fib-gallery>).

b) APT sample preparation

The APT sample preparation process was also carried out by FIB milling including:

- 1) The lift out extraction from the bulk material after protection of the region of interest (ROI) by Pt deposition.
- 2) The welding and cutting process on predefined tips.
- 3) the annular milling procedure to define the final shape of the tip, as shown in Fig. 3.12.

Fig. 3.12: FIB-based lift-out process and annular milling for needle preparation: (a) selection of a specific site for lift-out sample preparation and Pt capping of the ROI; (b) trenching on either side of the ROI to get a triangular wedge; (c) lift-out of the specimen using a nanomanipulator; (d) attachment of a specimen wedge on the microtip post; (e) one specimen wedge on the microtip post at the beginning of annular milling; (f) final needle specimen with <100 nm end diameter [97].

c) Micropillar preparation

The mechanical behaviour of selected alloy compositions within the inter-diffusion regions of interest in the diffusion couple was measured by micropillar compression. Square micropillars were utilized [98,99], because they allow for a more reliable slip trace measurement on the side surfaces while, simultaneously, yielding identical mechanical properties to cylindrical pillars [100]. Micropillar side lengths ranging from 2 to 7 μm were selected in order to investigate potential size effects. An aspect ratio between 2:1 and 3:1 (height: side) was used in all pillars with the aim of avoiding buckling effects during compression.

3.3 Nanomechanical testing techniques

Fig. 3.13: Example of micropillar milling process with the square $5\mu\text{m}\times 5\mu\text{m}$ size milling procedure. (a) The first rough milling with current 21 nA. (b) The second milling with current 9.3 nA. (c) The third milling with less current. (d) The last step for removing the taper with 80 pA.

Before milling the micropillars the diffusion multiple was first tilted 52° in order to place the specimen surface perpendicular to the ion beam. The longitudinal edge of the diffusion multiple was oriented horizontally. At the sites of interests, the following successive milling steps were carried out: (i) rough milling for the fast removal of the surrounding material (Fig. 3.13a); (ii) milling with smaller ion currents (9.3 and 2.5 nA) for a smoother approach to the final dimension of the micropillars (Fig. 3.13b and Fig. 3.13c); (iii) taper removal and surface polishing with an 80 pA ion current after tilting the sample to 53.5° and 50.5° , respectively; (iv) sample rotation of 90° and repetition of step (iii). A representative $5\times 5\times 10\mu\text{m}$ micropillar thus fabricated is shown in Fig. 3.13d. One edge of all the square pillars fabricated in this work was made parallel to the longitudinal edge of the diffusion multiple.

3.3 Nanomechanical testing techniques

3.3.1 Nanoindentation

The determination of the mechanical response of Mg-Zn alloys as a function of chemical composition based on diffusion couples required the use of a range of micro- and nanomechanical testing strategies. They include nanoindentation and micropillar compression, both *ex situ* and *in-situ* inside a scanning electron microscope. This section gives a general introduction to the different nano-mechanical testing methods and the testing equipment utilized in this work.

3.3 Nanomechanical testing techniques

Photographs of the Hysitron TI950 triboindenter system are shown in Fig. 3.14. The triboIndenter uses a vertical axial-loading system based on a piezoelectric force transducer and capacitance depth-sensing indenter head. The system is equipped with a (1) low-load transducer, (2) a high-load transducer, (3) an optical microscope and (4) a sample positioning stage, as shown in Fig. 3.14a. The low-load transducer can reach a maximum force of 12 mN with force resolution <1 nN and displacement resolution <0.02 nm. This transducer is also capable of measuring the stiffness continuously (nano dynamic mechanical module, nanoDMA mode) during testing. The high-load transducer reaches a maximum load of 1 N with force resolution <1 μ N and displacement resolution <0.1 nm. Finally, all the hardware is embedded on an active vibration isolation system and located in a thermal and acoustic enclosure designed to minimize vibrations, thermal drift and acoustic noise during testing. Additionally, a high temperature stage (x-Sol™) can be installed for high-temperature experiments, as shown in Fig. 3.14b.

Fig. 3.14: The Hysitron TriboIndenter platform employed in this work: (a) TI950, showing (1) the standard load transducer (2) high load transducer (3), optical camera and (4) sample stage. (b) High X-sol stage (x-Sol™).

3.3.2. Indentation creep

Indentation creep was used to study the creep behaviour in the Mg/Mg-Zn diffusion couple. Creep is essentially the time-dependent plastic response of a material under stress. In the case of depth-sensing indentation tests, the nominal pressure in the zone under the indenter is often very high, and can easily reach a few percent of the shear modulus of the material. Under these conditions, nearly all materials, including metals and even ceramics, are known to creep to some extent at low homologous temperatures. Depth-sensing indentation measurements can be conveniently applied to the study of strain-rate effects on deformation behaviour and the creep properties of materials in small volumes

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[36,38,101]. In uniaxial tensile creep tests, the steady-state creep behaviour of a wide range of materials can be described by a power-law equation of the type:

The strain rate and the equivalent flow stress can be described by equation (2.1), repeated here for the sake of clarity:

$$\dot{\epsilon} = A \left(\frac{GbD}{kT} \right) \left(\frac{\sigma}{G} \right)^n \exp\left(\frac{-Q}{RT}\right) \quad (3.1)$$

where $\dot{\epsilon}$ is the strain rate, σ the applied stress, n the stress exponent, Q the activation energy, k is the Boltzman constant, T the absolute temperature, G the temperature dependent shear modulus, D the diffusion rate, b the Burgers vector and A some pre-factor.

In this work, the Hysitron TI950 with nano-DMA mode was used for creep testing at room and high temperature. Weihs and Pethica [102] introduced a dynamic nanoindentation technique for conducting local long-term creep experiments. Using an alternating force signal, the contact stiffness S is continuously recorded during the indentation test. Whereas the indentation depth h recorded by the system is highly influenced by thermal drift, the contact stiffness is not, so the true contact area A_C can be reliably determined using Sneddon's equation:

$$A_C = \frac{\pi}{4\beta^2} \cdot \frac{S^2}{E_R^2} \quad (3.2)$$

The contact depth can be computed from the following analogy:

$$\dot{\epsilon}_c = \frac{\dot{h}_c}{h_c} \sim \frac{\dot{S}}{S} \quad (3.3)$$

while hardness can be continuously computed as:

$$H = \frac{P}{A_C} = P \cdot \frac{4\beta^2}{\pi} \cdot \frac{E_R^2}{S^2} \quad (3.4)$$

The hardness is directly related to flow stress through the constrain factor, $H = c \cdot \sigma_f$ ($\epsilon_{\text{rep-Berko}}=8\%$), where c is typically of the order of 2.8 for metals. Making an analogy with steady-state creep, then the strain rate sensitivity can be directly obtained from:

$$\dot{\epsilon} = K \cdot H^n = K \cdot H^{\frac{1}{m}} \quad (3.5)$$

$$m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}} \sim \frac{\partial \ln H}{\partial \ln \dot{\epsilon}} = \frac{1}{n} \quad (3.6)$$

3.3 Nanomechanical testing techniques

Based on this, the stress exponent n can be obtained from the slope of σ versus $\dot{\epsilon}$ in a log-log plot under isothermal conditions. Similarly, the activation volume can be determined from:

$$V^* = \frac{2.8 \times \sqrt{3} kT}{H} \left(\frac{\delta \ln \dot{\epsilon}}{\delta \ln H} \right) \quad (3.7)$$

Finally the activation energy Q can be calculated following the work by R. Alizadeh [103], plotting $\ln \left(\dot{\epsilon} * \frac{T}{G} \right)$ versus $1/T$ at constant σ .

3.3.3. Micro pillar compression

Two *in situ* nanomechanical testing systems have been employed in this work for the micropillar compression tests: the Hysitron Triboindenter TI950 and a Hysitron PI 87 platform using 10 μm diamond flat punch indenters, both at room and high temperature. The Hysitron Triboindenter TI950 was described in the previous section. The PI87 picoindenter is a depth-sensing mechanical test platform that was designed to be interfaced with SEM, enabling the *in situ* observation of microscale deformation at ambient or elevated temperatures. Furthermore, this indentation platform has a piezo-actuated stage with 5 degrees of freedom (X, Y, Z, rotation, and tilt), which allows for alignment correction between the sample and the flat punch indenter (Fig. 3.15). In this thesis, high temperature micropillar compression was carried out inside an SEM (EVO MA15, Zeiss) on the PI87 platform coupled with a temperature controller (Model 336, LakeShore). A high load transducer with a maximum force of 150 mN, a force resolution of 1 μN , and a displacement resolution of 0.1 nm was utilized. More details about the testing conditions are described in the corresponding chapters.

Fig. 3.15: The Hysitron Tribo Indenter nanoindentation platforms PI87 employed in this work.

3.4 Identification of active deformation mechanism

In the twinning favourable orientation, the deformation twinning was determined by Transmission Kikuchi Diffraction (TKD), schematically shown in Fig. 3.16, which offers near TEM resolution, enabling the analysis of the larger areas than it is possible by TEM [104,105]. This technique was developed to analyse materials with features smaller than could be accurately studied with standard EBSD. Among others, these features can include nanometre scale grains, small inclusions, and thin twins. Additionally, preparation of specimens for transmission electron backscatter diffraction (t-EBSD) requires the same processes as those for TEM, which produce samples thinner than ~200 nm.

Fig. 3.16: *Schematics of t-EBSD.*

Finally, for the determination of the dislocation Burgers vector, two-beam bright-field (TBBF), two-beam dark-field (TBDF) or weak-beam dark-field (WBDF) contrast was used in the TEM [95]. In particular, the 'g·b' visibility criteria was used to discern different types of dislocations in HCP lattice. Particularly, the $g = 0002$ diffraction condition is especially useful, as $\langle a \rangle$ type dislocations are invisible (with $g \cdot b = 0$), whereas only dislocations having a $\langle c \rangle$ component (i.e., $\langle c \rangle$ or $\langle c + a \rangle$ type) will be in contrast [73].

Chapter 4

Basal slip and tension twinning studied by nanoindentation

4.1 Introduction

This chapter summarizes the nanoindentation studies carried out in the Mg/Mg-Zn diffusion couple as a function of Zn content. The main body of literature on solid solution strengthening in Mg alloys relies on the mechanical behaviour of polycrystalline alloys [106–109]. As such, and considering the anisotropic behaviour of Mg alloys, most previous works study the coupled effect of alloying content on texture evolution, grain refinement and strengthening on the different slip and twinning modes. The work presented in this chapter constitutes a preliminary attempt to decouple these effects by studying the effect of Zn content on the nanoindentation behaviour within individual grains present in the diffusion couple. The objective was to eliminate the effect of texture and grain size, with the attempt of isolating the strengthening effect on the different slip and twinning modes active in Mg alloys.

To this end, quasi-static and long-term nanoindentation creep tests were performed at increasing temperatures (in the range between 25 °C and 300 °C) within individual grains of the Mg/Mg-Zn diffusion couple (i.e. maintaining the same crystal orientation), as a function of Zn content in the range between 0 to 2.2 at.%. The quasi-static nanoindentation tests served to elucidate solid-solution strengthening effects and the competition between basal slip and tensile twinning. Moreover, the nanoindentation creep tests contributed to understand the main deformation mechanisms controlling the creep strength of Mg-Zn alloys, a subject that is still controversial [36,110].

It should be stressed that the study of creep behaviour by nanoindentation tests is by no means a conventional methodology. The test involves measuring the increase in

4.2 Experimental procedure

indentation depth with time under a constant applied load [10]. As such, one of the main challenges faced on performing indentation creep experiments was the control of thermal drift, especially when the tests were carried out at elevated temperature. To overcome this problem, the final approach adopted in this work combined nano-indentation creep experiments with continuous stiffness measurements on the gradient composition spectra of the diffusion couple. The measurement incorporated a unique reference frequency technique for thermal drift correction during the course of an experiment, enabling long-duration creep tests.

4.2 Experimental procedure

The diffusion couples between the cast pure Mg and Mg-2.3 at. % Zn alloys were prepared following the procedure described in section 3.1. After metallographic preparation, the chemical composition profiles in the diffusion couple were measured by EPMA, while the crystallographic orientation of the grains was determined by EBSD, as explained in section 3.2. Nanoindentation was used in selected areas of the diffusion couple to determine the mechanical behaviour as a function of grain orientation and Zn content. A Hysitron TI950 Picoindenter equipped with a Berkovich diamond tip, described in 3.3.1, was used in all cases. Two types of nanoindentation experiments were conducted at room temperature: quasi-static indentation tests, to compute hardness and modulus, and constant load indentation creep tests, to measure the strain rate sensitivity. For each type of test, grids of 3×6 indentations performed, with the columns parallel to the interface in the diffusion couple, so that the 3 indentations in each row were made at the same Zn concentration. The spacing between indents in each direction was set to 50 μm to ensure no overlapping between their plastic zones.

The quasi-static indentation tests were performed in displacement control mode using a displacement rate of 800 nm/s up to the maximum displacement of 4000 nm. The load function used for the constant load indentation creep tests consisting of a loading rate of 0.6 mN/s up to a maximum load of 12 mN and a long holding time between 600 and 900 s, during which the increase of indentation depth was computed over time. The tests were performed at 25, 100, 200, and 300 °C in the same instrument using a diamond Berkovich indenter tip and an x-Sol[®] high temperature stage. Even though the thermal drift of the system was measured to be 0.1 nm/s at all temperatures, management of

thermal drift during the high temperature tests was challenging due to their long duration. To overcome this challenge, a dynamic creep testing technique was employed, whereby a small dynamic oscillation of 300 μN at a reference frequency of 220 Hz was superimposed onto the quasi-static load function, to measure the contact stiffness continuously throughout the test, with the aid of a lock-in amplifier. This approach relies on the relationship between contact area and contact stiffness to correct the indentation depth from thermal drift effects over long time periods. Following this approach, the strain rate sensitivity, activation volume and activation energies were computed following the methodology described in 3.3.2.

4.3 Results

4.3.1 Effect of Zn content on the room temperature hardness

Fig. 4.1 shows the detail of the area of the Mg-Zn diffusion couple used for the room temperature nanoindentation studies. According to the EBSD grain reconstruction in Fig. 4.1a, the two grains selected for the room temperature studies, with Euler angles of (9.3, 105.2, 14.1) and (38.1, 68.6, 6.9), had both a declination angle δ (defined as the angle between the indentation axis and the c-axis of the unit cell) of $70 \pm 5^\circ$. Fig. 4.1b shows that the Zn content varied between 0 and 2.2 at.% Zn in this area, while the SEM image in Fig. 4.1c demonstrates that the interface was clean of defects or pores coming from the diffusion bonding process. The nanoindentation hardness was strongly affected by the Zn content, as shown in Fig. 4.2, with the hardness varying 3-fold from pure Mg to Mg-2.2 at.% Zn, in agreement with previous results [26]. In order to elucidate the active deformation mechanisms, the indentation profiles were examined by SEM and EBSD.

Fig. 4.1: Detail of the area of the Mg/Mg-Zn diffusion couple used for the room temperature nanoindentation studies: (a) Grain reconstruction by EBSD (color code according to the inverse pole figure, IPF, of the surface normal); (b) composition profile measured by EPMA; and (c) SEM image of the area indicated by the rectangle.

4.3 Results

Fig. 4.2: *Hardness versus Zn content across the selected grains, all with a declination angle of 70° , in the diffusion couple.*

Fig. 4.3 displays SEM images and the corresponding EBSD maps for representative indentations as a function of Zn content. The SEM images showed evidence of basal slip traces in all cases. Basal slip traces were visible on both sides of the indents, but they were longer and more pronounced on one side than the other, as it is often seen for HCP metals [111]. Interestingly, the number of basal slip traces increased significantly with Zn content, as seen in the SEM images of Fig. 4.3.

Moreover, the SEM images revealed the presence of a two-fold sink in region around the indents, which is indicative of extension twinning when indenting grains with a high declination angle [112]. As a matter of fact, the EBSD maps show regions of large misorientation associated with the sink-in areas, that correspond to the activation of different twin variants in each case. Interestingly again, and as analysed in more detail below, the degree of sink-in and the extension of the twins seem to decrease significantly with Zn content.

Fig. 4.3: SEM images and the corresponding EBSD maps for representative 4000 nm deep indentations, all performed in grains with a declination angle of $\delta = 70 \pm 5^\circ$ for (a) 0 at.% Zn; (b) 0.25 at.% Zn; (c) 0.85 at.% Zn; (d) 1.69 at.% Zn; (e) 2.15 at.% Zn; and (f) 2.29 at.% Zn.

To prove this, the areas of the activated twin variants were carefully determined as a function of Zn content. Table 4.1 lists the 6 potential twin variants associated with extension twinning, while Table 4.2 summarizes the twin variants actually observed around the indents as a function of Zn content, determined based on the method of least misorientation between the Euler angle of matrix and the twin variant proposed by Zhang *et al.* [113].

4.3 Results

Table 4.1: List of possible extension twin variants.

No.	Twin direction	Twin plane
T1	$[1\bar{1}01]$	$(\bar{1}102)$
T2	$[\bar{1}101]$	$(1\bar{1}02)$
T3	$[10\bar{1}1]$	$(\bar{1}012)$
T4	$[\bar{1}011]$	$(10\bar{1}2)$
T5	$[01\bar{1}1]$	$(0\bar{1}12)$
T6	$[0\bar{1}11]$	$(01\bar{1}2)$

Table 4.2: Euler angles and twin variants of the twins identified in the vicinity of the indentations as a function of Zn content.

Euler angles of grain (°)	(at.% Zn)	Euler angles of activated twins (°)	Twin variants
9.3, 105.2, 14.1	0	124.9; 130.6; 25.9 59.8; 28.7; 52.4	T2 T5
	0.25	126.2; 130.1; 22.7 70.5; 26.3; 40.7	T2 T5
38.1, 68.6, 6.9	0.85	169.5; 34.1; 10.1 100.9; 124; 22	T6 T1
	1.69	104.2; 135.7; 23.6	T1
	2.15	106.5; 137.8; 25.5	T1
	2.29	110.2; 135; 30.6	T1

For instance, in pure Mg, two twin variants were activated corresponding to T2 and T5, covering a total twin area of $160 \mu\text{m}^2$. With increasing Zn content to 0.25 at.%, the same twin variants were found but they were significantly thinner and shorter, covering a smaller surface area around the indents (Fig. 4.3b). The trend continued with increasing Zn content, with only one twin variant present in the indentations with 2.29 at.%Zn, covering a negligible area around the indent, as seen in Fig. 4.3f. Even though the twins are 3D in nature, based on the fact that all indents were performed in grains with a similar orientation, it was hypothesized that the twin area on the indented surface was a good relative measurement of the amount of twinning in each case. However, since the hardness, and thus the indentation size, might vary with Zn content, the twin ratio [111], defined as the ratio between the total area of the twins and the area of the indentation imprint on the surface:

$$\text{Twin ratio} = \frac{\sum_i A_{Ti}}{A_{ind}} \quad (4.1)$$

was used to quantify the amount of twinning with Zn content. The results are summarized in Fig. 4.4, confirming that the amount of twinning decreases significantly with Zn content.

Fig. 4.4: The representative twin ratio measured as a function of Zn content for 4000 nm deep indentations in grains with a declination angle of $\delta = 70 \pm 5^\circ$.

In summary, the results presented so far indicate a higher activity of basal slip and a reduced activity of extension twinning with Zn content in indentations performed on grains with a declination angle of $\delta = 70 \pm 5^\circ$. Further evidence of the higher activity of basal slip with Zn content could be obtained from the Kernel misorientation maps plot in Fig. 4.5.

Fig. 4.5: Kernel misorientation maps as the function of Zn content overlaid with the image quality maps of the indentations.

4.3 Results

The Kernel misorientation maps illustrate the lattice rotation induced by basal slip with respect to the undeformed areas [111,114]. As measured in Fig. 4.6, the misorientation peaks at 0.5° for low Zn content, while the peak shifts to 1° for higher Zn contents.

Fig. 4.6: *The distribution of orientation deviation angle as a function of Zn content*

4.3.2 Effect of Zn content on the strain rate sensitivity at room temperature

Fig. 4.7 plots representative examples of indentation creep depth evolution with time as a function of Zn content for grains with the same declination angle of $\delta = 70 \pm 5^\circ$. The curves were mostly parabolic in nature and show a decreasing creep depth after 900 s with increasing Zn content, indicating that the addition of Zn improves the creep resistance.

Fig. 4.7: *Representative indentation creep curves as a function of Zn content in grains with $\delta = 70 \pm 5^\circ$.*

Following the analysis described in section 3.3.2, the strain rate sensitivity m was computed from the slope of the double logarithmic plot of hardness H versus strain rate $\dot{\epsilon}$, while the activation volume was determined from the slope of $\ln(\dot{\epsilon})$ versus H . The results are plot in Fig. 4.8, together with literature data for Mg alloys [115,116].

Fig. 4.8: (a) H - $\dot{\epsilon}$ represented in bilogarithmic coordinates; (b) Strain rate sensitivity (m) as a function of Zn content, compared with literature data [42,46]; (c) $\ln(\dot{\epsilon})$ versus H to determine the activation volume V^* ; (d) The activation volume V^* as a function of Zn content from current work and in [44].

The strain rate sensitivity m and activation volume V^* can provide insights on the rate controlling mechanisms in each case [117]. The strain rate sensitivity m at room temperature was found to decrease with Zn content, from 0.025 for pure Mg to 0.0025 for Mg-2.29 at.% Zn. In the same composition range, the activation volume was found to increase from 25 b³ to around 140 b³. As described above, the increase in Zn content suppresses twinning and promotes basal slip. Moreover, regarding the measured activation volume for Mg-2.29 at. %Zn, this is compatible with dislocation glide and/or cross slip, as summarized in table 4.4. Although cross slip might seem dubious at room temperature [6], the reduction in SFE induced by Zn alloying might explain the lower creep rate with

4.3 Results

increasing Zn content [118]. A lower stacking fault energy induces a large distance of separation between dissociated partials, and hence a lower rate of cross-slip [119].

Table 4.4 Activation volume of common deformation mechanisms [12].

Deformation mechanism	Activation volume (V^*)
Grain boundary diffusion	$1\sim 10b^3$
Dislocation nucleation	$1\sim 10b^3$
Confined layer slip	$10\sim 100b^3$
Cross slip	$10\sim 1000b^3$
Dislocation glide	$100\sim 1000b^3$
Dislocation forest cutting	$>1000b^3$

4.3.3 Effect of Zn content on creep deformation at elevated temperature

A different area of the diffusion couple was used for the elevated temperature nanoindentation studies, as shown in Fig. 4.9. The grain selected, with Euler angles of (125.4°, 93.4°, 52.6°), had a declination angle δ (defined as the angle between the indentation axis and the c-axis of the unit cell) of 86°. In this case, the composition range varied between pure Mg and Mg-0.77 at.% Zn to ensure that the Zn atoms remained in solid solution and to avoid the formation of Zn rich precipitates, during the long duration of the creep tests at elevated temperatures. By performing grids of indentations with the columns parallel to the diffusion couple interface, the indentation creep was studied for pure Mg, Mg-0.3 at. %Zn, Mg-0.56 at. % Zn and Mg-0.77 at. % Zn.

Fig. 4.9: Detail of the area of the Mg/Mg-Zn diffusion couple used for the high temperature nanoindentation studies: (a) Grain reconstruction by EBSD (color code according to the inverse pole figure, IPF, of the surface normal); (b) composition profile measured by EPMA; and (c) SEM image of the area indicated by the rectangle.

Representative creep displacement curves with time for Mg with different Zn contents in the temperature range between RT and 300 °C are shown in Fig. 4.10. As expected, increasing temperature increased the creep displacement in all cases. It is also

obvious from the creep curves that the creep strength increased with Zn content at all temperatures, in agreement with literature [120]. For instance, the creep displacement after 600 s at 300°C for pure Mg was 820 nm, while it decreased to 700 nm for Mg-0.77 at.% Zn.

Fig. 4.10: High temperature creep displacement evolution with time for (a) pure Mg; (b) Mg-0.33 at.% Zn; (c) Mg-0.56 at.% Zn and (d) Mg-0.77 at.% Zn.

The same analysis as that performed at room temperature in the previous section was carried out to determine the strain rate sensitivity and activation volumes, as a function of temperature and Zn content. Fig. 4.11 summarizes the strain rate sensitivity measurements. For pure Mg (Fig. 4.11a), the room temperature hardness was around 120 MPa at strain rates ranging from 10^{-3} s^{-1} to 0.1 s^{-1} , values that are consistent with literature in pure Mg [41,121,122] and with the results obtained in a grain with a different crystal orientation in the previous section. Increasing temperature induced a large drop in hardness for pure Mg. On the contrary, the hardness of Mg-0.77 at.% Zn (Fig. 4.11c) was much less sensitive to temperature up to 200 °C, but a large drop in hardness was seen when temperature increased to 300 °C. The activation volumes are summarized in Fig. 4.12.

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Fig. 4.11: Hardness versus strain rate in double logarithmic scale, and corresponding strain rate sensitivity, m , measured from the slope of the linear trends for (a) pure Mg; (b) Mg-0.33 at.% Zn; (c) Mg-0.56 at.% Zn and (d) Mg-0.77 at.% Zn.

Fig. 4.12: Summary of activation volumes at different temperatures, as a function of Zn content.

In order to elucidate the active deformation mechanisms, the creep indentations were also examined by SEM and EBSD [123]. According to the observations of Fig. 4.13a, the

room temperature deformation of pure Mg was controlled by the activation of T2 twin variant ($10\bar{1}2$)[$\bar{1}011$], and the associated sink-in pattern around the indent, indicating that twin boundary migration might play an important role during room temperature creep deformation for this grain orientation [124], similarly to the grain orientations studied before. However, as temperature increased, this twin variant and its associated sink-in pattern gradually disappeared, as shown in Fig. 4.13b to Fig. 4.13c, and evolved into a two-fold pile-up pattern with slip traces parallel to the basal planes, as pointed out by the red lines. This two-fold pile-up pattern has been reported to result from the combined action of basal and prismatic slip [125]. This transition from twinning to basal and prismatic slip dominated deformation is in agreement with literature observations showing that twinning activity decreases with temperature [126], while the combined basal and prismatic slip might be indicative of cross-slip, as the CRSS for prismatic slip decreases with temperature [127]. The transition from twin to slip dominated behaviour took place at a temperature between 200 °C and 300 °C, in agreement with literature [108].

Fig. 4.13: SEM images (above) and corresponding EBSD maps (below) of indents at (a) RT, (b) 100 °C, (c) 200 °C and (d) 300 °C for pure Mg.

Fig. 4.14 displays the corresponding SEM images and EBSD maps for indents made in Mg-0.56 at.% Zn. Contrary to pure Mg, basal slip traces, instead of twin activation, dominated the deformation pattern around the indents at room temperature (Fig. 4.14a), reinforcing the conclusion that Zn inhibits twin growth. Similarly to the case of pure Mg, however, with increasing temperature above 200 °C (Fig. 4.14c and d), the deformation pattern evolved into a two-fold pile-up pattern with slip traces parallel to the basal (red

4.4 Discussion

lines) and prismatic (green lines) planes. At even higher temperatures of 300 °C the slip traces adopted a wavy pattern (Fig. 4.14d), which has been previously related to the activation of extensive cross-slip between basal and prismatic slip planes [111, 123]. Therefore, an increasing temperature above 200°C seems to enhance the propensity for cross slip, also for Mg-0.56 at.% Zn.

Fig. 4.14: SEM images (above) and corresponding EBSD maps (below) of indents at (a) RT, (b) 100 °C, (c) 200 °C and (d) 300 °C for Mg-0.56 at.% Zn.

4.4 Discussion

4.4.1. Effect of Zn solid solution on the room temperature hardness

The results presented in section 3.3.1. demonstrate that Zn has a strong strengthening effect. However, the fact that increasing the Zn content leads to a higher activity of basal slip and a reduced activity of extension twinning in indentations performed on grains with a declination angle of $\delta = 70 \pm 5^\circ$, indicates that its effect is not equal for all deformation modes. Even though indentation imposes a multiaxial loading state, in order to rationalize the observations, it is illustrative to compute the Schmid factors (SF) of the different slip and twinning modes expected in Mg for the case of uniaxial loading in the indentation direction. For the selected grains, the maximum SFs for basal slip, prismatic slip, extension twinning and pyramidal slip are 0.24-0.33, 0.42-0.46, 0.32-0.37 and 0.47, respectively. Therefore, grains with a declination angle of $\delta = 70 \pm 5^\circ$ are preferentially

oriented for prismatic slip and extension twinning. However, if one takes pure Mg as a reference, the critical resolved shear stress (CRSS) for basal slip is extremely low (0.5 MPa), followed by extension twinning (7 MPa) and prismatic and pyramidal slip (40 MPa) [128]. Therefore, it is not surprising that for this grain orientation, the deformation around the indents is dominated by basal slip and extension twinning. The fact that basal slip seems to override extension twinning with increasing Zn content, to the extent that twinning is completely suppressed around the indents for 2.29 at.% Zn, qualitatively indicates that the Zn atoms induce a larger strengthening effect on extension twinning than for basal slip. This is in agreement with first principles calculations [80] and experimental observations in AZ31B alloys [129], addressing that solute atoms delay twin growth by hindering the expansion of twinning dislocation loops. However, any attempt to quantitatively estimate the solid solution strengthening effect of Zn from the nanoindentation tests remains elusive. Other micromechanical tests, like micropillar compression, should be better suited for this, as will be shown in the following chapters.

4.4.2. Effect of Zn content on creep activation energies as a function of temperature

The indentation creep results shown in section 4.3.3 demonstrate that small additions of Zn increase the creep strength of Mg, as reported in the literature [130]. The approach presented in section 3.3.3, based on the work of R.Mahmudi [39], was used to estimate activation energies from the high temperature creep data, normalized as shown in Fig. 4.15, where the slope is indicative of the stress exponent, n (the inverse of the strain rate sensitivity, m). From this, the strain rates for a constant $\ln(H/G) \approx 5$ were computed for each alloy composition, and used to produce plots of $\ln(\dot{\epsilon} \cdot T/G)$ versus $1/T$, from which the activation energy could be determined in each temperature range, as shown in Fig. 4.16. The results show two temperature regimes as a function of Zn content:

- In the low temperature regime (area shadowed in blue), the creep activation energy was ≈ 80 kJ/mol for pure Mg and diluted Mg-Zn alloys, which is in good agreement with the reported activation energy for grain boundary migration in Mg alloys [131,132]. This is in qualitative agreement with the deformation mechanisms observed around the indents at room temperature, dominated by twinning (Fig. 4.13a).
- While this behaviour seems to extrapolate to relatively high temperatures in pure Mg (200°C), Mg-Zn alloys go through a transition regime at intermediate temperatures (100-200°C) with much lower activation energies and activation

4.4 Discussion

volumes, which seems to be dominated by basal slip (Fig. 4.14b). In this regime, Zn alloying contributes to the suppression of twinning and to a substantial solid solution strengthening effect and an improved creep resistance, presumably because Zn atoms act as obstacles to dislocation glide. Additionally, the Zn atoms might segregate to defects such as dislocations, forming a Cottrell-type atmosphere around these defects, consequently retarding their motion due to viscous drag effects [1]. It is speculated that the reduced activation energy in this intermediate regime might be indicative of a dislocation climb controlled creep regime, as the activation energy for dislocation climb has been reported to decrease down to 66 kJ/mol in Mg-Zn-Zr [132], but further evidence is needed to demonstrate this.

- Finally, in the high temperature regime ($>200^{\circ}\text{C}$), all alloys converge to a relatively high activation energy, of the order of 150 kJ/mol. This is in good agreement with the activation energy reported for cross-slip in Mg, 147 kJ/mol [108]. This, together with the experimental observation of both basal and prismatic slip traces around the indents in this temperature range (Fig. 4.13d and Fig. 4.14d), constitutes a good indication that cross-slip between prismatic and basal planes becomes the rate controlling deformation mechanism at high temperatures. The main effect of Zn addition in this case is that creep rates are orders of magnitude lower for the Mg-Zn alloys than for pure Mg at the same stress level. It has been reported that the addition of Zn decreases the stacking fault energy [119] and consequently reduces the dislocation mobility, which might provide the enhanced creep resistance effect.

Fig. 4.15: Normalized $\ln(\dot{\epsilon}T/G)$ versus $\ln(H/G)$ at different temperatures to determine the stress exponent n for (a) pure Mg, (b) Mg-0.33 at.% Zn, (c) Mg-0.56 at.% Zn and (d) Mg-0.77 at.% Zn.

Fig. 4.16: Summary of determined activation energies at different temperature ranges, as a function of Zn content [132,133].

4.5 Conclusions

4.5 Conclusions

Nanoindentation was used to screen the effect of Zn content on the strength and creep resistance of Mg-Zn alloys using a high throughput methodology based on diffusion couples. The methodology is unable to provide quantitative estimates of Zn strengthening effects on the different deformation modes of Mg-Zn alloys but still the following conclusions could be drawn from this work:

- Zn atoms induce a strong solid solution strengthening effect with the nanoindentation hardness increasing 3-fold with increasing the Zn content from 0 to 2.2 at. %.
- For grains oriented favourably for extension twinning, increasing the Zn content from 0 to 2.2 at. % suppresses the activation of twinning in favour of basal slip, indicating that solid solution strengthening effects due to Zn alloying are larger for extension twinning than for basal slip.
- Zn alloying has also a strong effect on creep resistance, especially in the temperature range between RT and 200 °C. The strain rate sensitivity of pure Mg at RT is of the order of 0.025 and the rate controlling mechanism seems to be twin boundary migration, with a creep activation energy of ≈ 80 kJ/mol. Increasing the Zn content to 0.77 at. % Zn reduces the strain rate sensitivity abruptly by one order of magnitude to 0.0025, with a transition to a climb controlled dislocation glide regime, with a reduced activation energy.
- At temperatures above 200 °C, the strain rate sensitivity increases abruptly to 0.1 and deformation is dominated by basal and prismatic slip, entering a regime in which the rate controlling mechanisms is compatible with cross-slip with an activation energy of ≈ 150 kJ/mol.

Chapter 5

Effect of Zn distribution on basal slip

5.1 Introduction

The nanoindentation results presented in the previous chapter showed that increasing the Zn content in solid solution increases the CRSS for basal slip and tensile twinning in Mg-Zn alloys. Moreover, the results indicated that the Zn solid solution strengthening effect on extension twinning was larger than that on basal slip. However, it was concluded that nanoindentation was not able to isolate the strengthening effect of Zn in the different deformation modes controlling the mechanical behaviour of Mg-Zn alloys, due to the complex loading state introduced by this type of testing. Therefore, other micromechanical testing methods, like micropillar compression might be more suitable to isolate specific deformation modes. Among the different deformation modes (basal, prismatic and pyramidal slip and extension twinning), basal slip represents the softest deformation mode responsible for localization of deformation and the lack of ductility of Mg alloys. Therefore, basal slip strengthening might be one of the main contributions to the overall increase in yield strength and ductility in Mg-Zn alloys. For this reason, this chapter focuses on the effect of Zn on basal slip in these alloys.

Moreover, in the previous chapter, the strengthening effect of Zn was solely studied when the Zn atoms remained in solid solution into the Mg lattice. However, over the room temperature solubility limit, the precipitation process of Mg-Zn alloys is complex and involves the decomposition of the supersaturated solid-solution HCP phase to sequentially form G.P. zones, Zn rich clusters, β_1' (MgZn_2), β_2' (MgZn_2) and β (Mg_2Zn_3) [75,134,135]. The atomic distribution of the Zn atoms, i.e. whether the Zn atoms remain in solid solution into the Mg HCP lattice, their local order in terms of atomic clustering and/or the ultimate precipitation of second-phase particles will also have a strong influence on the CRSS for basal slip in Mg-Zn alloys, that has not been studied in detail so far as a function of Zn content.

In this context, the diffusion couple high-throughput approach presented in this thesis was used to carry out an in-depth study of the effect of Zn content and atomic distribution on basal

5.2 Experimental procedure

slip. For this, Mg/Mg-Zn diffusion couple were subjected to three different thermal histories, with the objective of inducing a different atomic distribution of the Zn atoms. More specifically, the diffusion couple were studied in the as-quenched (AQ) state, after natural or room temperature aging (RA) and after peak aging (PA) at high temperature. Specific grains in the diffusion couple, preferentially oriented for basal slip, were selected for micropillar compression studies both at 298 K (25 °C) and 373 K (100 °C). The micropillar compression studies, together with careful microstructural characterization of the deformed pillars by SEM, APT and TEM, allowed extracting interesting conclusions on the effect of Zn content and its distribution on basal slip in Mg-Zn alloys. This information is important for the design of new Mg alloys with improved strength and ductility.

5.2 Experimental procedure

5.2.1 Materials

The starting material was the Mg/Mg-2.3 at.%Zn diffusion couple, processed as described in section 3.1. After the diffusion annealing step carried out at 400°C for 336 hours in vacuum, the diffusion couples were subjected to three different metallurgical conditions to induce a different distribution of the Zn solute atoms: as-quenched (AQ) condition; room temperature aged (RA) condition by maintaining the specimen at room temperature for 1000 h; and peak aged (PA) condition, by thermally treating the diffusion couple at 200°C for 10 h. The distribution of the Zn solute atoms in each metallurgical condition was studied by APT and TEM, as described in section 3.3.2.

Fig. 5.1: The composition profile (measured by EPMA) as a function of diffusion distance along the black line, superimposed on the grain orientation map (measured by EBSD, colour code according to the inverse pole figure, IPF, normal to the surface) in one of the areas of the Mg-Zn diffusion couple used in this study.

5.2.2 Micropillar compression tests

Grains that were preferentially oriented for basal slip were identified from the EBSD maps of the diffusion couples. Table 5.1 lists the three grains under study in each of the metallurgical conditions. As summarized in this table, the maximum SF for basal slip for the selected grains, considering a loading direction parallel to the surface normal, was close to the maximum value of 0.5 in all cases, while the SF for extension twinning was always substantially lower, favouring therefore the activation of the first deformation mode in detriment of the second.

Table 5.1: The maximum SF for basal slip and tension twinning in the selected grain.

Condition	Euler angle (°)	SF _{basal slip}	SF _{Twinning}
As-quenched (AQ)	(30.8, 44.8, 50.3)	0.49	0.23
RT aged (RA)	(117.9, 33.2, 55.7)	0.45	0.35
Peak aged (PA)	(7.9, 137.0, 57.9)	0.49	0.26

The micropillars, with a square cross-section to facilitate slip trace identification, were machined by focused ion beam (FEI Helios Nano lab 600i) milling using the methodology described in section 3.2.3. The side lengths of the cross-section of the micropillars was varied from 3 to 7 μm in order to investigate potential size effects. An aspect ratio between 2:1 and 3:1 (height to side dimension) was used in all cases with the aim of avoiding buckling effects during compression. This aspect ratio range is commonly utilized in micropillar studies. The micropillars were carefully characterized by SEM imaging before and after testing, to evaluate their initial and final shape after deformation.

Pillar compression experiments were carried both *ex situ* and *in situ* at 298 K (25 °C) and 373 K (100 °C) at a strain rate of 10^{-3} s^{-1} , using the apparatus described in section 3.3. The load-displacement curves were first corrected by applying the Sneddon correction [136] in order to account for the extra compliance resulting from the elastic deflection of the bulk material surrounding the micropillars. The corrected curves were then transformed into engineering stress (σ)-strain (ϵ), considering the initial cross section and the height of the micropillars. From these curves, the yield stress was measured as the 0.5% offset yield stress. The Young's modulus was estimated from the upper portion of the unloading segment of the curves.

Slip traces at the surface of the micropillars were carefully examined by high resolution SEM in order to determine the active slip systems. Transmission electron microscopy (TEM) was used to analyse the internal dislocation structures developed after mechanical testing in selected micropillar. A trenching-and-lift-out focused ion beam (FIB) technique was adopted

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to extract a lamella which was thinned to approximately 100 nm for electron transparency, following the procedure described in section 3.2.3. TEM observation was carried out in a Talos F200X microscope operated at 200 kV.

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5.3.1 Distribution of the Zn solute atoms as a function of metallurgical condition

Fig. 5.2a shows a high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) image, together with the chemical distribution EDS map (shown in Fig. 5.2b.) in the AQ condition for an area with a local chemical composition of Mg-2 at.% Zn. The images show that the Zn atoms remain in solid solution, without the formation of second-phase precipitates. The atoms seemed to be homogeneously distributed. However, it should be stressed that the resolution of the TEM is not sufficient to evaluate the possible clustering of the Zn atoms.

For the RA condition, Zn clusters/ precipitates are seen in Fig. 5.2c and d. They were small, apparently spherical in shape, with an average size less than 10 nm, as shown in Fig. 5.3a. For the PA condition, however, the precipitates adopted a rod-shape morphology, with the elongated axis aligned along the *c*-axis of the matrix, as shown in Fig. 5.2e and f and Fig. 5.3b. The average length and diameter of the rod-shape precipitates were 95 ± 36 nm and 11 ± 3 nm, respectively, with the length ranging between 30 nm and 140 nm. The volume fraction of precipitates was 1.8%, following the methodology of Wang *et al.* for the quantification of the precipitates [137]. The average spacing between precipitates in the basal plane was 9.9 ± 4.5 nm. Overall, the precipitates had an average aspect ratio (length over diameter) of ≈ 9 , which is very close to the results reported by Wang and Stanford for alloys of similar composition and comparable aging conditions [137].

Fig. 5.2: (a-c) HAADF STEM image (left) and EDS map (right) for (a, b) AQ condition (c, d) RA condition and (e, f) PA condition.

Fig. 5.3: (a) and (b) show bright field (BF) TEM micrographs taken along the $[11\bar{2}0]$ zone axis for the diffusion couple in the RA (25°C for 1000 h) and PA (200°C for 10 h) conditions in an area with a local chemical composition of Mg-2 at.% Zn, respectively. The insets show the selected area electron diffraction (SAED) patterns of the underlying Mg matrix, with the arrow pointing to the direction of the $[0001]$ c-axis in each case.

It was not possible to analyse the chemical composition and crystal structure of the precipitates by TEM because of their small diameter. As explained in section 3.1, it has been proposed [138] that the decomposition of the supersaturated solid-solution matrix phase reportedly involves the formation of G.P zones, Zn rich clusters, rod-shape β'_1 (MgZn₂), plate-shaped β'_2 (MgZn₂), and stable β (Mg₂Zn₃). The formation of G.P zones, which are described as coherent disks formed on $(0001)\alpha$, has not been supported by direct experimental evidence so far [1]. Therefore, based on the accepted precipitation sequence in literature, the small spherical shape particles found in the RA condition should correspond either to Zn rich clusters or embryos of β'_1 (MgZn₂) precipitates. For the PA condition, however, based on their morphology, the precipitates are identified as β'_1 (MgZn₂) because of their rod shape parallel to the c axis of the Mg matrix, as shown by the SAED pattern in Fig. 5.3b. This Laves phase has a HCP crystal structure, with the following orientation relationship: $(0001)_{\beta'_1} \parallel (11\bar{2}0)_{Mg}$ and $[11\bar{2}0]_{\beta'_1} \parallel [0001]_{Mg}$ [4,134,137,139]. The a-axis of β'_1 precipitate grows parallel to the c-axis of the magnesium matrix and the c-axis of β'_1 is parallel to one of the three equivalent $[11\bar{2}0]$ directions in the matrix. The spacing along the a-axis of β'_1 closely matches the spacing along the c-axis of the alloy matrix giving rise to a low energy coherent β'_1 /Mg interface that explains the rod-shape. No evidence of disk-shaped β'_2 phase (MgZn₂) precipitates, which grows with a habit plane $(0001)_{\beta'_2} \parallel (0001)_{Mg}$, was found in either aged condition.

5.3.2 Micropillar compression results

The mechanical properties of the Mg-Zn alloys for the different metallurgical conditions were measured by means of micropillar compression tests at 25°C and 100°C. In general, the reproducibility of the tests was excellent, as shown in Fig. 5.4, where representative engineering resolved shear stress (based on the SF reported in Table 5.1)-engineering strain curves, $\tau_{RSS}-\epsilon$, are plotted for all conditions for pillars of Mg-2 at.% Zn with diameters of 5 and 7 μm . In order to obtain the bulk properties of metallic alloys from micropillar compression tests, it is important to demonstrate that they are not influenced by the micropillar size. Previous studies in Mg-Al and Mg-Zn alloys showed that generally, for basal slip oriented micropillars, size effects diminish for pillar sizes larger than 5 μm [65]. This is clearly demonstrated in Fig. 5.4, especially for the RA and PA conditions. While in the AQ condition, Fig. 5.4a and b, a residual size effect is observed between 5 and 7 μm pillars, the differences are negligible for the RA condition (Fig. 5.4c and d) and the PA condition (Fig. 5.4e and f). This is probably because in the precipitation hardened conditions the length scale that controls the mechanical behaviour is the precipitate spacing, which is much smaller than the micropillar dimension [140].

The $\tau_{RSS}-\epsilon$ curves in Fig. 5.4 show very similar features, regardless of the metallurgical condition and temperature. There was an initial elastic region, up to the yield point. The slope of the initial elastic loading was reproducible in most cases and mostly parallel to the slope of the final unloading, which is a good indication of the good alignment achieved between the flat punch and the pillar head. The average CRSS for the AQ condition was relatively lower (10 MPa) than those of the RA and PA conditions (15 MPa and 60 MPa, respectively), indicating that precipitation strengthening was more effective than solid solution strengthening in all cases. The shape of the curves after the initial yield, was also remarkably different in each case. The curves corresponding to the AQ condition (Fig. 5.4 a and b) were jerky, which is the typical behaviour encountered in micropillars as a result of the sudden activation of dislocation sources in localized slip planes. Negligible strain hardening was found in this condition and temperature had little effect on flow stress. The behaviour for the RA condition (Fig. 5.4 c and d) was similar, but at a substantially higher flow stress. However, the jerky behaviour was less pronounced for the RA and the degree of strain hardening up to an engineering strain of 5% was slightly higher than for the AQ condition.

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Fig. 5.4: The resolved shear stress–strain curves for Mg-2 at.% Zn for (a) AQ at RT; (b) AQ at 100 °C; (c) RA, at RT; (d) RA, at 100 °C; (e) PA, at RT; (f) PA, at 100 °C.

Finally, the main differences were found for the PA condition (Fig. 5.4 e and f). Not only the yield stress was substantially higher than in the previous cases, but the τ_{RSS} - ϵ curves were continuous, with no sudden load drops, representative of a more uniform behaviour. Moreover, the strain hardening rate after the initial yield was much higher than in the previous conditions,

indicating a higher rate of forest dislocation hardening [140]. Finally, and contrary to the previous conditions, the testing temperature seemed to have a strong influence, with the yield stress decreasing substantially from RT to 100 °C. This reduction is surprising, as precipitate strengthening is normally considered to be independent of temperature in so far the precipitates are stable, and will be discussed further below.

5.3.3 Deformation mechanisms

The shape of the deformed pillars and the corresponding TEM images of their longitudinal sections lifted-out by FIB milling are shown in Fig. 5.5. for each condition. The inserts correspond to the SAED patterns, indicating the orientation of the HCP Mg lattice in each case. The orientation of the slip traces confirmed the activation of basal slip in all cases, as expected from the chosen grain orientations and the SF analysis in Table 5.1. No twinning activity was observed in the TEM in any case. The number and size of basal slip traces in each condition correlate well with the shape of the τ_{RSS} - ϵ curves. In the AQ and RA conditions, strain localized in a discrete number of slip traces along the length of the pillar. The results suggest that the strain bursts are associated with the activation of discrete dislocation sources in adjacent basal slip planes giving rise to dislocation avalanches that exit at the walls of the micropillars, contributing to the progressive formation of slip steps of different intensity, as can be seen in the deformed pillars of Fig. 5.5a and c. On the contrary, the pillars deformed in the PA condition, Fig. 5.5 e and f, displayed a uniform strain distribution, with only one apparent basal slip trace. This, together with the shape of the τ_{RSS} - ϵ curves, suggest that the precipitates present in the PA condition do not only contribute to a higher CRSS for basal slip, but their strong interaction with the basal dislocations contributes to stop the dislocation avalanches and to diminish the localization of strain in a few slip bands, eliminating the jerky behaviour and resulting in an increase in the storage of forest dislocations that contribute to the observed strain hardening.

Fig. 5.5: The shape of the deformed pillars (left) and the corresponding TEM image of a longitudinal section (right) of the deformed pillar prepared by FIB for the (a, b) AQ; (c, d) RA and (e, f) PA conditions. The inserts correspond to the SAED pattern, indicating the orientation of the HCP Mg lattice in each case.

5.3.4 Distribution of the Zn solute atoms and their interaction with the basal dislocations

In order to gain a better understanding on the interaction of basal dislocations with the Zn solute atoms in each metallurgical conditions. APT specimens were extracted by FIB from deformed pillars following the procedure described in section 3.2.3. Unfortunately, no clear evidence of this interaction was obtained from this analysis. Nevertheless, the distribution of the Zn atoms in the APT specimens confirmed the TEM results described above. In the AQ condition, the Zn solute atoms were in solid solution in the supersaturated Mg-2 at.% Zn. No direct evidence of short-range clustering was obtained; instead the Zn atoms seemed homogenously dispersed, as seen in Fig. 5.6a. After room temperature aging for 1000 h, direct evidence of Zn clustering was observed, as shown in Fig. 5.6b, where small Zn clusters, presumably embryos of the β_1' (MgZn_2) precipitates, could be clearly observed.

Fig. 5.6: APT analysis of the (a) AQ condition; (b) RA condition. The green colour represents the Zn atoms. The sequence of images reveals the evolution of Zn distribution from a homogenous distribution in the AQ condition to short-range Zn rich clusters in the RA condition. The dash lines indicated the position of the basal slip trace.

TEM analysis of the deformed pillars, however, showed a clearer evidence of the type of dislocation-solute interaction occurring in each condition. Fig. 5.7a shows a TEM BF image of one slip trace in Mg-2 at.% Zn in the AQ condition deformed at 100 °C. No $\langle c+a \rangle$ dislocations were observed with $g=(0002)$ in the zone axis $[2\bar{1}\bar{1}0]$ condition, indicating no $\langle c+a \rangle$ dislocation activation. A detailed STEM image of the slip trace in Fig. 5.7b showed bright particles decorating the slip trace, that, according to the EDS maps of Fig. 5.7c and d, corresponded to Zn clusters. This analysis demonstrates the tendency of the Zn atoms to segregate and cluster upon interaction with the basal dislocations during deformation. The results were similar both in pillars deformed at RT and 100 °C. Solute segregation in the basal slip traces is expected to exert additional drag effects on the movement of basal dislocations, similarly to the observed pinning of twin boundaries by the segregation of solute atoms in Mg-Nd and Mg-Ag alloys [141], which inhibits twin growth. However, this constitutes the first experimental evidence of such segregation induced drag effects on the movement of basal dislocations in solid solution strengthened Mg-Zn alloys.

Fig. 5.7: TEM analysis of one slip trace in Mg-2at.% Zn in the AQ condition: (a) TEM BF image along $[2\bar{1}\bar{1}0]$ axis with the $g=(0002)$ condition.; (b) HAADF STEM image and corresponding EDS compositional maps of (c) Mg and (d) Zn.

Fig. 5.8: TEM BF images under different diffraction conditions in Mg-2 at.% Zn deformed at 100 °C in the AQ state to reveal the dislocation character of the array of dislocations pointed by the arrow: (a) $[2-1-10]$ zone axis with diffraction vector $g1 = [01-12]$; $[1-21-3]$ zone axis with (b) $g2 = [1101]$; (c) $g3 = [01-11]$ and (d) $g = [01-11]$. According to the $g \cdot b = 0$ invisibility criterion, the array of dislocations correspond to $\langle a \rangle$ dislocations with Burgers vector $b = \langle 1-210 \rangle$.

Interestingly, the TEM BF images of Fig. 5.8 show the presence of an array of dislocations under different diffraction conditions, as pointed by the arrow. The imaging conditions in Fig. 5.8 clearly reveal that the array of dislocations correspond to $\langle a \rangle$ dislocations gliding on basal planes in response to the applied stress. Since they are visible in all conditions, the Burgers vector must be $b = \langle 1\bar{2}10 \rangle$. The fact that the spacing between the dislocations in the array is uniform might indicate a low energy configuration due to their interaction with the Zn clusters.

Fig. 5.9: TEM analysis of slip traces in Mg-2at.% Zn in the RA condition deformed at 100 °C: (a) TEM BF image; (b) HAADF STEM image and corresponding EDS compositional maps of (c) Mg and (d) Zn.

In the case of the RA condition, Fig. 5.9 shows TEM images of the interaction between the Zn rich clusters with basal slip planes in pillars deformed at 100 °C. The images showed that the pre-existing Zn rich clusters interact with the gliding dislocations on the basal planes. Additionally, Zn atoms tended to segregate on the basal slip planes, similarly to the AQ condition. Imaging of the basal $\langle a \rangle$ dislocations under different diffraction conditions in Fig. 5.10 revealed a higher density of gliding dislocations than in the AQ condition, indicating a stronger interaction of the Zn atoms with the basal dislocations, in agreement with the higher CRSS and strain hardening capacity and the smaller stress drops observed in the τ_{RSS} - ϵ curves. Additionally, Fig. 5.10a-c show numerous segments of $\langle a \rangle$ dislocations perpendicular to the basal planes. It was not possible to elucidate whether such jogs formed by cross-slip onto prismatic planes and/or a climbing process, but they should be presumably a consequence of

the barrier exerted by the Zn rich clusters on the gliding dislocations. Such jogs, rather immobile under the applied stress, surely contribute to the higher CRSS measured in the RA condition.

Fig. 5.10: TEM BF images in $[10-10]$ zone axis under different diffraction conditions in Mg-2 at.% Zn in the RA state: (a) low magnification, showing a high density of basal slip traces; (b) and (c) higher magnification showing jogs on the basal slip traces; (d) $g=[0002]$.

Finally, Fig. 5.11 and Fig. 5.12 show TEM BF images of pillars of Mg-2 at.% Zn in the PA condition, deformed at RT and 100 °C respectively. No significant differences were observed in both cases, indicating that despite the large drop in CRSS from RT to 100 °C in this case, the deformation mechanisms remain unchanged with temperature. In both cases, the rod-like β_1' (MgZn_2) precipitates are sheared by the gliding basal dislocations, as shown in Fig. 5.11 and Fig. 5.12a at RT, and in Fig. 5.12d at 100 °C. Therefore, it was concluded that

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precipitation strengthening corresponded to the case of shearable precipitates, rather than the Orowan type hardening induced by impenetrable particles. A high density of gliding basal dislocations was seen in the deformed pillars as indicated by the arrows in Fig. 5.12b and e, in agreement with the high strain hardening rate observed in the micropillar compression tests.

Fig. 5.11: TEM analysis of slip traces in Mg-2at.% Zn in the PA condition deformed at RT (a) TEM BF image; (b) HAADF STEM image and corresponding EDS (c) Mg and (d) Zn compositional maps.

Fig. 5.12: TEM BF images in $[2-1-10]$ zone axis under different diffraction conditions in Mg-2 at.% Zn in the PA condition: (a) low magnification, (b) high magnification and (c) SAED at RT; (d) low magnification, (e) high magnification and (f) SAED at 100 °C.

5.4 Discussion

The results indicate that the yield stress of Mg-Zn alloy micropillars favourably oriented for basal slip depends strongly on the Zn content and the solute distribution, which in turn depends on the thermal history. The CRSS for basal slip in Mg-Zn is plotted in Fig. 5.13 versus the Zn content for each metallurgical condition, both at RT and 100 °C. The CRSS were obtained from the 7 μm wide micropillars. On top of the results presented above for Mg-2 at.% Zn for all metallurgical conditions, additional tests were carried out at 1.5 %at. Zn content within the diffusion couple for the AQ condition. Literature data for the CRSS for basal slip obtained from micropillars and from macroscopic tests in single crystals in Mg-Zn alloys for different precipitation conditions are also included in the graph for the sake of comparison. Fig. 5.13 demonstrates that the high throughput approach followed in this work yields direct results comparable to those obtained in macroscopic samples, corroborating the validity of the approach. Overall, Fig. 5.13 indicates that solid solution is quite effective on strengthening basal slip, especially in the supersaturated regime, but Zn clustering effects induced by room

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temperature aging provide twice as much strengthening for the same Zn content. Moreover, the formation of rod-like β_1' (MgZn_2) precipitates by peak aging at 200 °C provides a 4-times more strengthening effect than solid solution. Nevertheless, it is interesting to address that both solid solution and solute cluster strengthening are relatively athermal, while precipitation strengthening strongly decreases by 20 % at 100 °C. In the following, the main findings for each metallurgical conditions are thoroughly discussed.

Fig. 5.13: RSS for basal slip determined from the 7 μm pillars as a function of Zn content for the AQ, RA and PA conditions. Comparison with literature data from micropillar compression and in situ neutron diffraction studies are also included [75,77,142].

5.4.1 Solid solution strengthening in the CRSS for basal slip in Mg-Zn alloys

A reasonable way of quantifying the strengthening effect of Zn is to compute the difference between the CRSS for basal slip determined for Mg-Zn and the CRSS for basal slip determined for pure Mg using an identical method (micropillar compression of 7 μm wide micropillars) [65]. The results are plotted in Fig. 5.14, only considering the AQ and RA conditions, to quantify the solid solution strengthening effect of Zn. The results are compared with literature results using tensile testing in macroscopic single crystals [63,64] Both data at 25 °C and 100 °C are plotted in each case but they are indistinguishable because the results were independent of temperature. Unfortunately, past fundamental studies in macroscopic single crystals only covered dilute alloys, i.e., concentrations of less than 0.5 at.% in alloying content, within the solubility limit at room temperature. An exception is the work of Chun and Byrne [143], which determined the CRSS for basal slip in supersaturated Mg-2 at.% Zn single crystals, and the results are also plotted in Fig. 5.14.

Fig. 5.14: Strengthening in CRSS, $\Delta\text{CRSS} = \text{CRSS}_{\text{alloy}} - \text{CRSS}_{\text{Mg}}$, from compression tests in micropillars of $7 \times 7 \mu\text{m}^2$ cross-section at RT and 100 °C. Some relative results from literature are also included [64,88,142].

The strengthening due to the solid solution can be modelled using the Labusch model (see section 2.2) according to:

$$\Delta\tau = \tau_{\text{alloy}} - \tau_{\text{Mg}} = Kc^{2/3} \quad (5.1)$$

where c is the solute element content (in at. %) and K is a constant that depends on the alloying element and temperature [143]. The experimentally determined strengthening for supersaturated Mg-Zn at both temperatures corresponds to $K = 3.5 \text{ MPa}^{-1}$, in the AQ condition and $K = 6.7 \text{ MPa}^{-1}$, in the RA condition. The results are in good agreement with previous bulk data [64,143], but the strengthening slope K in the supersaturated regime is much larger than that found for diluted alloys, $K = 1.7 \text{ MPa}^{-1}$ [64]. Therefore, the evidence suggests that the solid solution strengthening effect of Zn is far more efficient in super-saturated alloys than in diluted alloys. Among others, the tendency of Zn atoms for solute clustering [143] and short range order [144] have been considered as possible reasons for this behaviour. As a matter of fact, the APT and TEM studies presented in section 5.3.4 showing the tendency of Zn to segregate and cluster confirm that this is the case. The short range clustering observed on the slip trace in Fig. 5.7 and Fig. 5.9 indicate that the spatial fluctuations enable the dislocations to find low-energy configurations [43,145]. It has been reported that the local deviations from the mean concentration leading to SRO (or its counterpart, short range clustering) are a feature of concentrated solid solutions, the intensity of these deviations being a function of the magnitude and sign of the interaction energy between solute and solvent atoms [146].

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5.4.2 Precipitation strengthening in the CRSS for basal slip in Mg-Zn alloys

As shown in Fig. 5.13, precipitation strengthening by rod-like β_1' (MgZn_2) precipitates in the peak aged condition provides by far the most efficient strengthening effect in the CRSS for basal slip. Assuming the strengthening mechanisms are additive, according to the micropillar compression results, the precipitation induced strengthening τ_p for Mg-2 at.% Zn in the peak aged condition could be estimated from:

$$\tau_p = \tau_{crss} - \tau_{Mg} - \tau_{ss} \quad (5.2)$$

where τ_{crss} is the CRSS measured by micropillar compression, τ_{Mg} is the one corresponding to pure Mg and τ_{ss} corresponds to the solid solution strengthening due to the Zn that remains in solid solution after the precipitation process. Considering that τ_{crss} was 60 MPa and 40 MPa at RT and 100 °C respectively, that $\tau_{Mg} = 7$ MPa and that $\tau_{ss} = 1$ MPa at most (diluted region of Fig. 5.14), then $\tau_p = 52$ MPa at RT and 32 MPa at 100 °C. The results are comparable to literature data by Wang *et al.* [5] in Mg-5wt.% Zn.

The high temperature dependency of the precipitation induced strengthening seemed surprising. In order to rule out the potential effect of precipitate coarsening during the tests at 100 °C, the dimensions of the precipitates after high temperature testing were also measured, yielding identical results to those found after the peak aging treatment, as shown in Fig. 5.15 a. Moreover, some micropillars were tested at RT after being heated to 100°C yielding identical results to those initially tested at RT as shown in Fig. 5.15b. These results ruled out any potential coarsening of the precipitates as the possible origin of softening at high temperature.

Fig. 5.15: (a) Length and diameter of the precipitates in the PA condition before and after heating at 100 °C; (b) The representative engineering stress-strain curves of PA Mg-2at.% Zn alloy deformed at RT, 100°C and RT after heating to 100 °C

Fig. 5.11 and Fig. 5.12 at RT and 100 °C, respectively, clearly show that the precipitates are sheared by the basal dislocations. Therefore, an Orowan type strengthening mechanism can be ruled out in this case, as would be the case for impenetrable precipitates. Moreover, the softening observed at elevated temperature would not be compatible either, as Orowan stresses should be relatively athermal except for the temperature dependence of the shear modulus. On the contrary, it can be concluded that the current case corresponds to the precipitation strengthening regime where the precipitates are shearable by the dislocations. This might not be surprising considering the semicoherent $\alpha(\text{Mg})/\beta_1'(\text{MgZn}_2)$ interface and the fact that the most dense plane, $(2\bar{1}\bar{1}0)$, of the β_1' precipitates is parallel to the basal plane of the Mg matrix, facilitating the shearing process [138].

For the case of the shearable particles, a number of possible mechanisms can be operative/controlling. These include stacking fault energy mismatch (most relevant to the case of disordered precipitates with the same crystal structure as the matrix), interface creation, modulus mismatch, coherency strain, and anti-phase domain boundary (APB) order strengthening [147]. Due to their coherence with the matrix, order strengthening is expected to be the dominant mechanism for $\beta_1'(\text{MgZn}_2)$. Anti-phase boundaries (APB) are generated if the particles are sheared by gliding dislocations. The APB energy per unit area on the slip plane, γ_{APB} , represents the force per unit length opposing the dislocation cutting through the particle [147,148]. Strong order strengthening effects have also been found in Mg-Li alloys [87], Mg-Al [87] and WE43 Mg alloys [147].

The strengthening expected for the rod like shearable precipitates [74,87,137,147,149] was given in equation (2.8), repeated here for the sake of clarity:

$$\tau_p = \frac{\gamma_{APB}}{2b} \left(\frac{d}{\left(\frac{0.953}{\sqrt{f}} - 1 \right) d} - f \right) \quad (5.3)$$

where d is the diameter of the precipitates in the basal plane and f is the volume fraction of precipitates. Using the diameter of the precipitates 11 ± 3 nm and the measured volume fraction 1.8%, the APB energy γ_{APB} was estimated to be 183 mJ/m² and 123 mJ/m² at RT and 100 °C, respectively. No literature data was found for the γ_{APB} in $\beta_1'(\text{MgZn}_2)$, but a negative temperature dependence of the APB energy [150] has also been reported for Fe-Al [151] and Ni-Al [152,153] intermetallics.

5.5 Conclusions

5.5 Conclusions

The effect of Zn distribution on the CRSS for basal slip in Mg-2at.% Zn alloys has been evaluated by micropillar compression in the AR, RA and PA conditions. The key findings can be summarized as follows:

- The following precipitation sequence has been found. The Zn solute atoms are homogeneously dispersed in solid solution in the AQ state, with some tendency to cluster specially for the supersaturated 2 at.% Zn content. Room temperature aging for 1000 h leads to clustering of the Zn atoms into spherical shape Zn rich particles with sizes < 10 nm. Peak aging at 200°C for 10 h results in rod-shape precipitates of β_1' (MgZn₂), aligned along the <c> axis of the α -Mg matrix, with a mean diameter and length of 11 ± 3 nm and 95 ± 36 nm, respectively.
- Zn clustering and short range order seems to play an important role on solid solution strengthening of basal slip supersaturated Zn alloys. The strengthening for 2 at.%Zn in the AQ conditions sums up to $\approx 6 \pm 1$ MPa for the AQ condition and $\approx 11 \pm 1$ MPa for the RA condition, much larger than what is expected for diluted Mg-Zn alloys. Solid solution strengthening is temperature independent between RT and 100 °C and contributes to negligible strain hardening.
- A strong strengthening for basal slip by β_1' (MgZn₂) precipitates was found in the PA condition. The strengthening for 2 at.% Zn amounts to $\approx 52 \pm 2$ MPa at RT, but decreases to $\approx 32 \pm$ MPa at 100 °C. Precipitation strengthening leads to larger strain hardening due to the increase in forest dislocation hardening induced by the precipitates. The β_1' (MgZn₂) are shearable by the precipitates and order strengthening is expected to be the dominant mechanism responsible for the strong precipitation hardening.

Chapter 6

Effect of Zn distribution on tension twinning

6.1 Introduction

After basal slip, twinning deformation is the second softest deformation mode in Mg alloys, and therefore, is the other elementary carrier of plastic deformation, especially along the $\langle c \rangle$ axis [154]. The most commonly observed twinning mode in Mg alloys is $\{10\bar{1}2\}$ tension or extension twinning [155]. Twinning deformation strongly affects the mechanical behaviour of Mg alloys, specially their yielding [156] and work hardening behaviour through their interaction with lattice dislocations, other twins, solute atoms [80] and precipitates [89,154]. The latter might be beneficial for increasing the strengthening and ductility of Mg alloys [157], but can also induce anisotropy and/or compression-tension asymmetry to the polar character of twinning. Moreover, as twinning involves the rotation of a discrete volume of the lattice, the mechanical behaviour is also influenced by the activation of other deformation modes, such as basal or pyramidal slip in the twinned region. Solid solution and/or precipitation hardening are also expected to affect the twinning behaviour, especially twin growth, as solute atoms and precipitates can strongly affect twin boundary (TB) migration. For instance, Zn atoms, with smaller atomic radius than Mg atoms, tend to segregate to the compression region of dislocation cores in grain boundaries, whereas Ca or Y (with a larger atomic radius than Mg) tend to segregate to the extension region [44,158,159]. Therefore, Zn atoms are expected to interact strongly with TB.

The effect of Zn alloying on the twinning behaviour has only been covered in detail in previous studies up to concentration levels below 0.5 at% Zn [69,160], within the solid solubility range at room temperature [5,6], and well below the Zn content of commercial alloys, which can reach 4.5 at% Zn (11 wt.% Zn) [146]. In the case of concentrated as-

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extruded and precipitation hardened Mg-6 wt.% Zn binary alloys, previous studies have suggested that precipitates impair twin boundary migration [24,137], similarly to the case of Mg reinforced with Y_2O_3 [161]. However, modelling studies by Fan *et al.* [154] found that precipitates are engulfed by the growing twins and rotate elastically with the lattice. In summary, only a limited number of studies have been performed to quantify the effect of Zn content and distribution on twinning deformation in Mg-Zn alloys.

This work tries to answer the pressing need for quantitative describing of effect of the Zn distribution on twinning deformation in Mg-Zn binary alloys by combining diffusion couples with micropillar compression studies. For this, a complete study of deformation twinning was carried out using micropillar compression of grains favourably oriented for twinning in Mg-2 at.% Zn in three different metallurgical conditions: as-quenched (AQ), room temperature aged (RA) for 1000 h and peak aged (PA) at 200 °C for 10 h. In particular, two aspects were studied: (i) the effect of Zn distribution on the CRSS for twin nucleation and growth and (ii) the work hardening behaviour of the twinned re-oriented pillars. The deformed pillars were carefully studied by TKD-assisted slip trace analysis, APT and TEM characterization. Large differences were observed on twin nucleation, twin growth and post-twinning work hardening behaviour as a function of metallurgical condition.

6.2 Experimental procedure

6.2.1 Materials

The starting material was the Mg/Mg-2.3 at.% Zn diffusion couple, processed as described in section 3.1. After the diffusion annealing step carried out at 400°C for 336 hours in vacuum, the diffusion couples were subjected to three different metallurgical conditions to induce a different distribution of the Zn solute atoms: as-quenched (AQ) condition; room temperature aged (RA) condition by maintaining the specimen at room temperature for 1000 h; and peak aged (PA) condition, by thermally treating the diffusion couple at 200°C for 10 h. The distribution of the Zn solute atoms in each metallurgical condition was studied by APT and TEM, as the results were presented in section 5.3.

Fig. 6.1 shows the microstructure of the Mg/Mg-Zn diffusion couple under study. After the diffusion annealing step, carried out at 400 °C for 336 hours in vacuum, the grains were as large as 500 μm , and the Zn content varied within the diffusion region in the range between 0 and 2.5 at. %, as shown in the composition profiles measured by

EPMA. The study was carried in two orientations that were favourably oriented for twinning, but that showed a distinct post-twinning behaviour. For grains labelled G1, as that shown in green in Fig. 6.1 a, the loading axis was close to the $\langle a \rangle$ axis, $[11\bar{2}0]$, while for grains labelled G2, as that shown in blue in Fig. 6.1 (b), the loading axis was close to the normal of one of the prismatic planes, $[10\bar{1}0]$.

Fig. 6.1: Composition profile (measured by EPMA), as a function of diffusion distance in superimposed with the IPF map of the direction perpendicular to the surface, two representative areas of the Mg-Zn diffusion couple. In (a), the loading axis of the grain in green is parallel to $[11\bar{2}0]$, while in (b) the loading axis of the grain in blue is parallel to the normal to one of the prismatic planes $[10\bar{1}0]$.

As summarized in Table 6.1, all G1 and G2 grains displayed declination angles (angle between the surface normal and the $\langle c \rangle$ axis) $> 70^\circ$. In all cases, the maximum SF, close to ≈ 0.5 , corresponded to prismatic slip, while the S.F. for tension twinning were slightly different: ≈ 0.37 for G1 and ≈ 0.5 for G2. The reason why these two grain orientations were selected to study twinning was that, even though both deformed initially by twinning, they showed a distinct post-twinning deformation behaviour, as will be shown below.

6.2 Experimental procedure

Table 6.1: The grains, favourably oriented for twinning selected in each case and their corresponding maximum SF for basal slip, prismatic slip and tension twinning.

Alloy	Euler angles (°)	Maximum SF		
		Basal slip	Prismatic slip	Tension twinning
Pure Mg	G1 (146.9, 111.4, 13.6)	0.33	0.43	0.35
	G2 (143.6, 81.3, 26.8)	0.13	0.44	0.48
Mg-2%Zn (AQ)	G1 (32.6, 77.1, 3.9)	0.21	0.44	0.37
	G2 (136.3, 83.6, 27.5)	0.09	0.44	0.49
Mg-2%Zn (RA)	G1 (145.5, 110.6, 14.4)	0.23	0.44	0.36
	G2 (166.9, 97.0, 21.3)	0.14	0.48	0.48
Mg-2%Zn (PA)	G1 (134.5, 92.6, 1.5)	0.04	0.44	0.38
	G2 (39.6, 89.1, 35.4)	0	0.47	0.49

6.2.2 Micropillar compression

The micropillars, with a square cross-section to facilitate slip trace identification, were machined by focused ion beam (FEI Helios Nano lab 600i) milling using the methodology described in section 3.2.3. The side lengths of the cross-section of the micropillars was varied from 3 to 7 μm in order to investigate potential size effects. An aspect ratio between 2:1 and 3:1 (height to side dimension) was used in all cases with the aim of avoiding buckling effects during compression. This aspect ratio range is commonly utilized in micropillar studies. The micropillars were carefully characterized by SEM imaging before and after testing to evaluate their initial and final shape after deformation.

Pillar compression experiments were carried at 298 K (25 °C) at a strain rate of 10^{-3} s^{-1} , using the apparatus described in section 3.3. The load-displacement curves were first corrected by applying the Sneddon correction [136] in order to account for the extra compliance resulting from the elastic deflection of the bulk material surrounding the micropillars. The corrected curves were then transformed into engineering stress (σ)-strain (ϵ), considering the initial cross section and the height of the micropillars.

6.2.3 Analysis of the deformation mechanisms

Slip traces at the surface of the micropillars were carefully examined by high resolution SEM in order to determine the active slip systems. Transmission Kikuchi Diffraction (TKD) was used to study twin activation. As schematically illustrated in Fig. 6.2, a trenching-and-lift-out focused ion beam (FIB) technique was adopted to extract a

lamella which was thinned to approximately 100 nm for electron transparency, following the procedure described in section 3.2.3. TKD was carried out in a FEI Helios Nano lab 600i SEM equipped with an Oxford EBSD camera.

Fig. 6.2: (a) Schematic illustration of the orientation of the lift-out lamella which respected to the deformed pillar. (b) SEM image of one of the electron transparent lamella.

The dislocation structures were studied by TEM, using a FEI Talos F200X microscope operated at 200 kV. Two-beam bright-field (TBBF), two-beam dark-field (TBDF) and/or weak-beam dark-field (WBDF) imaging techniques were used to obtain dislocation contrast [73]. In addition, the “ $g \cdot b = 0$ ” invisibility criteria was used to discern the different types of dislocations present in the HCP lattice: $\langle a \rangle$ dislocations, with $b = \frac{1}{3}\langle 11\bar{2}0 \rangle$, $\langle c \rangle$ dislocations with $b = [0001]$, and $\langle c + a \rangle$ dislocations, with $b = \frac{1}{3}\langle 11\bar{2}3 \rangle$ [19,73]. In particular, the $g = [0002]$ diffraction condition was especially useful, as $\langle a \rangle$ dislocations are invisible (with $g \cdot b = 0$), whereas only dislocations having the $\langle c \rangle$ component (i.e., $\langle c \rangle$ or $\langle c + a \rangle$ type) will be in contrast [35].

6.3 Results

6.3.1 Twinning deformation in pure Mg.

First, the results obtained in the pure Mg side will be presented, since significant differences were found between the G1 and G2 orientations, that are indicative of the anisotropic behaviour of Mg. As summarized in Table 6.1, both grains, G1(146.9, 111.4, 13.6) and G2 (143.6, 81.3, 26.8), had a declination angle $\Phi > 60^\circ$, and therefore, are both favourably oriented for tension twinning [162,163]. G1 was oriented such that the loading axis was close to $[11\bar{2}0]$, while for G2 the loading axis was close $[10\bar{1}0]$.

6.3 Results

a) $[11\bar{2}0]$ loading axis

Representative stress-strain curves for pillars of different sizes are plotted in Fig. 6.3. In all cases, yielding was followed by a strain softening stage after the peak stress, that increased with pillar size reduction from 60 MPa for a pillar size of 7 μm to 107 MPa for a pillar size of 3 μm , respectively. Analysis of the deformed pillars in Fig. 6.4 revealed the same deformation morphology irrespective of pillar size. The deformed pillars were severely bent, as indicated by the blue lines at the sides of the pillars. Clear slip traces (as indicated by the orange solid line) were visible within the bent regions. The slip traces seemed to be straight within these regions, but accumulated a large curvature at the shear bands denoted by the green dashed lines. The latter indicates that the slip traces were activated first, followed by the bending of the pillars, forming what appeared to be a kink band. From the slip trace orientation at the upper part of the pillar (not bent) the slip traces were compatible with basal slip.

Fig. 6.3: Representative engineering stress-strain curves for loading axis close to $[11-20]$ ($\Phi \approx 70^\circ$) in pure Mg, as a function of pillar size.

It is important to address that bending during micropillar compression could be indicative of incorrect alignment between the head of the pillar and the flat punch, as reported in LiF [164]. However, the latter could be easily ruled out in the current case, as misalignment errors usually manifest with very different slopes during the elastic loading and unloading sections of the compression curves, and this was not the case in the curves of Fig. 6.3. In order to further elucidate the formation sequence of the kink bands, different 3 μm micropillars were subjected to compression up to increasing strains of 2% (corresponding to the peak stress) and 5%, 12.5% and 20% (within the strain softening

stage), as shown in Fig. 6.5. The corresponding surfaces of each deformed micropillar are gathered in Fig. 6.6. According to this sequence of events, plastic deformation initiated by the activation of basal slip and the pillars remained straight up to the peak stress, at a total strain of 2%. At this point, the pillars started to bend, inducing the strain softening observed in the compression curves. Using the slip traces as deformation marks, bending induced a severe lattice rotation within the centre of the pillars forming the kink band.

Fig. 6.4: SEM images of deformed pillars for loading axis close to $[11-20]$ ($\Phi \approx 70^\circ$) in pure Mg, as a function of pillar size: (a) $3\mu\text{m}$, (b) $5\mu\text{m}$ and (c) $7\mu\text{m}$.

The lattice rotation accumulated at the boundaries of the kink band, across which the lattice rotation increased with applied strain to reach a value as large as $\approx 20^\circ$, for a total strain of 20%.

Fig. 6.5: Engineering stress-strain curves of $3\mu\text{m}$ pillars deformed to different levels of total strain, from 2 to 20%.

6.3 Results

Fig. 6.6: SEM images for the four sides of the pillars deformed up to a total strain of: (a) 2%; (b) 5%; (c) 12.5% and (d) 20%. All the pillars are 3 μm .

In order to understand how such a large lattice rotation could be accommodated across the kink band, EBSD was performed on the sides of one of the pillars deformed up to a total strain of 5%. Fig. 6.7a shows the SEM image of the back side of the pillar (side 4 according to convention described in Fig. 6.2a), where the basal slip traces are clearly visible. The EBSD map of Fig. 6.7b confirms that the original parent orientation is maintained within the kink band, but that the large lattice rotation across the kink boundaries, are accommodated by the nucleation of two narrow twin bands, denoted twin1 and twin2. The misorientation profile in Fig. 6.7c showed that the misorientation of both twin1 and twin2 with the parent orientation was 90° , confirming that they correspond to $\{10\bar{1}2\}$ tension twins.

Fig. 6.7: EBSD analysis of one of the sides of a pillar deformed to 5%. (a) The back side (side 4) of the pillar, with the basal slip traces marked in orange; (b) EBSD map showing two narrow bands with a different crystal orientation at the boundaries of the kink band. (d) The misorientation along the black dash line, indicating the nucleation of two narrow twins at the boundaries of the kink band.

The deformation sequence observed might be understood considering that, according to Table 6.1, the SF for basal slip, prismatic slip and tension twinning are 0.36, 0.43 and 0.35, respectively. Since the CRSS for prismatic and pyramidal slip are much higher (>40 MPa) [33,34,68,165]) than for basal slip (~ 0.5 MPa) [31,166]) and extension twinning (7–12 MPa) [18,24,31,112,176,192], a competition between basal slip and extension twinning occurs. Basal slip accommodates most of the plastic strain initially, but since the basal planes are oriented at 20° with respect to the loading axis, they rotate leading to an initial strain hardening. When the level of applied stress is sufficiently high, two twin band nucleate leading to the formation of a kink band and the severe bending of the pillar, triggering the strain softening behaviour. The two twin bands remain relatively thin during deformation and accommodate the large lattice rotation at the boundaries of the kink band. Kink deformation has been also reported in polycrystalline Mg-Y and Mg-Zn-Y alloys, and it is also profusely observed in HCP Zn single crystals [29,167–173].

b) $[10\bar{1}0]$ loading axis

Fig. 6.8 plots representative engineering stress-strain curves as a function of pillar size for a grain oriented with the loading axis close to $[10\bar{1}0]$. The declination angle was similar to the previous case ($\Phi \approx 81^\circ$), but when the HCP lattice is loaded along the normal to one of the prismatic planes, the compression behaviour is remarkably different. For all pillar sizes, the stress increased elastically, followed by a large strain burst at an applied strain of 1%. The peak stress at the strain burst was larger the smaller the pillar size. The flow stress after the peak stress remained relatively constant up to an applied

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strain of 4-6%, followed by a strong strain hardening regime. Fig. 6.9 shows the deformed pillars, demonstrating that all pillars deformed in the same way irrespective of pillar size.

Fig. 6.8: Representative engineering stress- strain curves for loading axis close to $[10\bar{1}0]$ ($\Phi \approx 81^\circ$) in pure Mg, as a function of pillar size.

Fig. 6.9: SEM images of deformed pillars for loading axis close to $[10-10]$ ($\Phi \approx 81^\circ$) in pure Mg, as a function of pillar size: (a) $3\mu\text{m}$, (b) $5\mu\text{m}$ and (c) $7\mu\text{m}$. The dashed lines indicate the more pronounced slip traces found in the pillars

In order to gain a better understanding of the deformation mechanisms for this loading orientation, the deformed pillar shown in Fig. 6.10 (a) was FIB milled to extract an electron transparent lamella, as indicated by the dashed line. The transmission EBSD (t-EBSD) map of Fig. 6.10 (b) clearly shows that the entire volume of the pillar had twinned, except for a small band at the base of the pillar that retained the parent orientation, as demonstrated by the misorientation profile along the left edge of the pillar plotted in Fig. 6.10 (c). The loading axis changes from $[10\bar{1}0]$ in the parent orientation to $[10\bar{1}30]$ in the twin, which has a misorientation angle of 2.9° with respect to the $[0001]$ direction of the HCP lattice.

Fig. 6.10: (a) SEM image of the 3 μm pillar deformed with loading axis close to $[10\bar{1}0]$, indicating the relative orientation of the TKD lamella extracted by FIB; (b) t-EBSD map, and corresponding misorientation profile along the left edge, showing that the entire pillar volume had twinned, except for a small band at the base of the pillar that retained the parent orientation. The EBSD maps indicates that the slip trace corresponds to basal slip in the twinned region.

Even though the twin is favourably oriented for pyramidal slip and that the SF for basal slip is relatively low, it is clear from the slip traces in Fig. 6.9 that basal slip activates in the twin, owing to the low CRSS for basal slip in pure Mg. However, the DF TEM images of Fig. 6.11, with diffraction condition $g=(\bar{2}110)$, show a large density of $\langle c+a \rangle$ dislocations in the twinned region, indicating that both pyramidal and basal slip activate in the twin, which might explain the large work hardening behaviour observed for large applied strains.

Contrary to the $[11\bar{2}0]$ loading orientation, the $[10\bar{1}0]$ loading orientation has been profusely studied in the past in pure Mg and the observations fully agree with these previous studies [24,174–176]. It is remarkable that two loading directions with similar declination angles ($70\text{--}80^\circ$) show a completely different behaviour owing to the strong anisotropy of pure Mg and the competition between basal slip and extension twinning. The following sections focus on the effect of Zn alloying under different metallurgical conditions (solid solution, room aging and peak aging) on the deformation of these two grain orientations.

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Fig. 6.11: DF-TEM images of the deformed pillar in Fig. 6.10 with diffraction condition $g=(-2110)$ in (a) twinned region and (b) parent orientation. (c) and (d) are the corresponding diffraction patterns.

6.3.2 Twinning deformation in Mg-2 at.% Zn in the AQ condition

Representative engineering stress-strain curves for as-quenched Mg-2 at.% Zn as a function of pillar size compressed with the loading axis close to $[11\bar{2}0]$ and $[10\bar{1}0]$ are shown in Fig. 6.12a and b, respectively. From the analysis of Zn distribution in section 5.3.1, the Zn atoms in the as-quenched supersaturated Mg-2 at.% Zn remain in solid solution, without the formation of second-phase precipitates.

Fig. 6.12: Representative engineering stress-strain curves for as-quenched Mg-2 at.% Zn as a function of pillar size, compressed with loading axis close to (a) $[11\bar{2}0]$ and (b) $[10\bar{1}0]$.

The behaviour is remarkably different to that of pure Mg, particularly on the $[11\bar{2}0]$ loading direction, even though the SF for the different deformation modes were similar to the pure Mg case (Table 6.1), demonstrating the strong effect of the Zn solid solution on the deformation along directions favourably oriented for twinning. In this case, both the $[11\bar{2}0]$ and $[10\bar{1}0]$ loading directions began with an elastic linear loading that ended with an abrupt strain burst at a total strain of 1% strain. The main difference between both

loading orientations was found in the post-yielding deformation. While the flow stress after the peak stress plateaued at a relatively constant level even up to a total strain of 12-14% for the $[11\bar{2}0]$ orientation, a strong strain hardening was found for the $[10\bar{1}0]$ orientation after a total strain of 4%, similarly to the case of pure Mg, but at higher flow stresses. The flow stress was relatively size independent for the 5 and 7 μm micropillars, but a large size effect of the type “smaller is stronger” was found for the 3 μm micropillars.

In order to determine the operating deformation mechanisms, electron transparent lamellae were extracted from selected micropillars for TKD and TEM analysis. Fig. 6.13a shows a $[11\bar{2}0]$ oriented 7 μm deformed micropillar. Contrary to the pure Mg case, the Zn solute atoms prevented the activation of basal slip in the parent orientation and the subsequent bending of the micropillar (cf. with Fig. 6.6). On the contrary, the deformed pillar was almost completely twinned, except for small volume at the top and bottom of the pillar.

Fig. 6.13: (a) SEM image of the 7 μm deformed pillar in the as-quenched Mg-2 at.% Zn alloy compressed along the $[11\bar{2}0]$ direction ; (b) TEM cross-section and corresponding SADP for the (c) parent and (d) twinned orientation; (e) t-EBSD map.

From the TEM image of Fig. 6.13 b it is unclear whether only one twin nucleated and grew or two twins nucleated at the top and bottom of the pillar and grew to meet at the central part, but the final result was that the complete pillar was twinned in a single variant, as demonstrated in the diffraction patterns of twin and parent orientation in Fig. 6.13c and d and the t-EBSD map of Fig. 6.13e. Subsequently, the pillar deformed by the activation of basal slip in the twinned region, as demonstrated by the slip trace marked by the dashed orange lines. This is not surprising since the maximum SF for basal slip

6.3 Results

within the twinned region was computed to be 0.37 (Table 6.2). Finally, the TEM images of Fig. 6.14 show limited activity of $\langle c+a \rangle$ dislocations (red arrows) in the twinned region and profuse basal slip traces and extended basal stacking faults (orange arrows), presumably due to the reduction in SFE induced by the Zn atoms [70,177,178].

Fig. 6.14: TEM images showing the dislocation structure after deformation in the as-quenched Mg-2 at.% Zn alloy compressed along the $[11-20]$ direction: (a) BF image in diffraction condition $g= (0002)$ showing $\langle c+a \rangle$ dislocations (red arrows) and (b) DF image in diffraction condition $g= (01-10)$ showing basal dislocations and planar stacking faults (orange arrows).

Contrary to the $[11\bar{2}0]$ oriented pillars, the operating deformation mechanisms for the $[10\bar{1}0]$ oriented $7\text{ }\mu\text{m}$ deformed micropillar in the as-quenched Mg-2 at.% Zn alloy were identical to those found in pure Mg for the same orientation. After the strain burst, the entire pillar adopted the twin orientation, as shown by TEM (Fig. 6.15b) and t-EBSD (Fig. 6.15c), and basal slip traces (marked by the orange dashed lines) indicated the activation of basal slip on the twinned region. Further TEM analysis of the dislocation structures confirmed profuse activity of basal $\langle a \rangle$ dislocations and $\langle c+a \rangle$ pyramidal dislocations, which is not surprising, considering that the maximum SF for basal slip was only 0.12 and the SF for $(11\bar{2}2)[\bar{1}\bar{1}23]$ pyramidal slip was 0.48 within the twinned region (Table 6.2). It was concluded therefore that, in the case of as-quenched Mg-2 at.% Zn alloys, the two $[11\bar{2}0]$ and $[10\bar{1}0]$ orientations favorably oriented for twinning showed a much more similar behaviour than in the case of pure Mg, with the main difference being the post-twinning behaviour. While in the former orientation, strain after twinning was accommodated by basal slip only, giving rise to a regime with a relatively constant flow stress, in the latter, strain was accommodated both by basal and pyramidal slip, explaining the high strain hardening regime after twinning.

Fig. 6.15: (a) SEM image of the 7 μm deformed pillar in the as-quenched Mg-2 at.% Zn alloy compressed along the $[10-10]$ direction; (b) TEM cross-section and (c) t-EBSD map.

Fig. 6.16: TEM images showing the dislocation structure after deformation in the as-quenched Mg-2 at.% Zn alloy compressed along the $[10-10]$ direction: (a) BF image and (b) DF image in diffraction condition $g= (0002)$ showing $\langle c+a \rangle$ dislocations.

Table 6.2: SF of basal, prismatic and pyramidal slip in the twins for each loading direction. G1' indicates the twin orientation after loading along $[11-20]$ and G2', the same after loading along $[10-10]$.

Alloy	Twinned orientation ($^\circ$)	Maximum SF		
		Basal slip	Prismatic slip	Pyramidal slip
Pure Mg	G1' (146.9, 111.4, 13.6)	0.43	0.1	0.41
	G2' (16.8, 96.8, 26.8)	0.28	0.05	0.49
Mg-2%Zn (AQ)	G1' (18.3, 71.6, 56.3)	0.37	0.04	0.45
	G2' (174.6, 84.6, 6.7)	0.12	0.05	0.48
Mg-2%Zn (RA)	G1' (23, 83.4, 30.7)	0.35	0.04	0.46
	G2' (8.8, 98, 30.3)	0.19	0.04	0.49
Mg-2%Zn (PA)	G1' (19.2, 106.5, 56.5)	0.38	0.08	0.45
	G2' (177.5, 86.3, 44.3)	0.07	0	0.47

6.3 Results

6.3.3 Twinning deformation in Mg-2 at.% Zn in the RA condition

Representative engineering stress-strain curves for Mg-2 at.% Zn, room temperature aged for 1000 h, compressed with the loading axis close to $[11\bar{2}0]$ and $[10\bar{1}0]$ are shown in Fig. 6.12a and b, respectively, as a function of pillar size. From the analysis of Zn distribution in section 5.3.1, the Zn atoms in the RA condition segregate to form spherical shape Zn rich clusters with dimensions smaller than 10 nm, in agreement with previous observations [179]. The stress-strain curves were very similar to the as-quenched Mg-2 at.% Zn (cf. with Fig. 6.12) for both orientations: an initially elastic linear loading segment up to an applied strain of 1%, followed by a sudden strain burst indicating the nucleation and propagation of deformation twins. Again the flow stress on the $[11\bar{2}0]$ oriented pillars remained relatively constant after twinning, while the $[10\bar{1}0]$ oriented pillars showed a marked strain hardening behaviour after twinning. The major qualitative difference with the as-quenched conditions was found to be the relatively smaller size of the strain bursts after twinning, which might be indicative of a more gradual process of twin growth.

Fig. 6.17: Representative engineering stress-strain curves for room aged Mg-2 at.% Zn as a function of pillar size, compressed with the loading axis close to (a) $[11\bar{2}0]$ and (b) $[10\bar{1}0]$.

The SEM images of Fig. 6.18 also indicate a more uniform deformation of the pillars as suggested by the smaller strain bursts in the stress-strain curves. The same slip traces as those seen in the AQ condition (cf. with Fig. 6.13 and Fig. 6.15) were found, i.e. basal slip traces (marked by the orange lines) in both orientations, indicating activation of basal slip in the twinned regions. However, the slip traces were more uniformly distributed than in the previous cases, in which basal slip localized in just a few slip planes. The latter might be an indication of a stronger interaction of basal dislocations with the Zn rich

clusters in the RA condition, in agreement with the conclusions obtained in the previous chapter.

Fig. 6.18: SEM images of the 7 μm deformed pillars compressed along the (a) $[11-20]$ direction and the (b) $[10-10]$ direction. The orange lines marked the basal slip traces in each case.

Provided the deformation behaviour was similar to the previous case, no further TEM analysis is included in this case. However, advanced TEM analysis provided a possible physical explanation for the more gradual twin growth process suggested by the stress-strain curves. One example is shown in Fig. 6.19 for the deformed 5 μm $[11\bar{2}0]$ oriented micropillar in Fig. 6.19a, from which the TEM lamella shown in Fig. 6.19b was lifted out. The HAADF STEM image in Fig. 6.19c and the EDS Zn elemental map in Fig. 6.19d revealed preferential Zn segregation at the twin boundaries, indicating that the Zn rich clusters might slow down twin boundary migration.

Fig. 6.19: (a) 5 μm $[11-20]$ oriented deformed micropillar. The orange line marks the orientation of the basal slip traces in the twinned pillar; (b) TEM lamella lift out from the deformed pillar showing the twinned volume. The blue dashed lines indicate the position of the twin boundaries; (c) HAADF STEM image and (d) Zn EDS elemental map, showing Zn segregation at one of the twin boundaries.

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6.3.4 Twinning deformation in Mg-2 at.% Zn in the PA condition

Representative engineering stress-strain curves for Mg-2 at.% Zn in the peak aged condition (200 °C for 10 h), compressed with the loading axis close to $[11\bar{2}0]$ and $[10\bar{1}0]$ are shown in Fig. 6.20a and b, respectively, as a function of pillar size. From the analysis of Zn distribution in section 5.3.1, the Zn atoms in the PA condition gave rise to rod-shape β_1' (MgZn₂) precipitates, with the long axis oriented parallel to the $\langle c \rangle$ axis of the HCP Mg lattice. The stress-strain curves were remarkably different to the ones measured in the AQ (cf. with Fig. 6.12) and RA (cf. with Fig. 6.17) conditions for both orientations, indicating a strong interaction of the twinning process with the β_1' (MgZn₂) precipitates. After the linear elastic loading segment, a more gradual initial yielding was observed at an applied strain of 2%. The initial yielding, which is associated with twin nucleation, occurred at stresses that were significantly higher than in the AQ and RA conditions. Moreover, the post-yielding behaviour was also more gradual in both cases, suggesting a more sluggish twin growth process. Interestingly, the differences between the $[11\bar{2}0]$ and $[10\bar{1}0]$ oriented stress-strain curves in Fig. 6.20a and b, respectively, were smaller than in the previous cases, indicating a less anisotropic behaviour, presumably due to the interaction of the β_1' (MgZn₂) precipitates with basal slip and twinning deformation.

Fig. 6.20: Representative engineering stress-strain curves for peak aged Mg-2 at.% Zn as a function of pillar size, compressed with the loading axis close to (a) $[11\bar{2}0]$ and (b) $[10\bar{1}0]$.

The morphology of the deformed pillars agreed with the expected behaviour from the shape of the stress-strain curves. For instance, Fig. 6.21a shows the SEM image of one of the 7 μm deformed pillars compressed along the $[11\bar{2}0]$ direction. No slip traces could be seen on the surface of the pillars. Instead, the contrast marked by the blue arrows suggests the nucleation of several twins. The TEM image of a FIB lamella extracted from

the same pillar in Fig. 6.21b confirmed the nucleation of several twins in different locations, all with the same crystal orientation, as revealed by the SAED patterns of Fig. 6.21c and d. Therefore, it appears that the β_1' (MgZn_2) precipitates exert a strong pinning effect on the twin boundaries, so that the twinning process takes place by the nucleation of several small twins instead of the nucleation and growth of one or two twins, as was the case in the same orientation for the AQ and RA conditions. The latter also explained why no basal slip traces were observed on the pillars after twinning.

Additional TEM images, taken at different diffraction conditions, of the area circled in blue in Fig. 6.21 b, are gathered in Fig. 6.22. Fig. 6.22a–e revealed profuse activity of both $\langle a \rangle$ basal and $\langle c+a \rangle$ pyramidal dislocations. The arrows point to locations where dislocations are clearly pinned by the presence of precipitates, revealing their strong interaction, not only with the TBs, but also with the gliding dislocations. The latter confirmed that precipitates do not only limit twin growth but they are also responsible for the activation of basal and pyramidal slip in the twinned regions, explaining the strong strain hardening behaviour found for the two orientations under study.

Fig. 6.21: (a) SEM image of the 7 μm deformed pillar in the peak-aged Mg-2 at.% Zn alloy compressed along the $[11-20]$ direction; (b) TEM cross-section and corresponding SADP for the (c) parent and (d) T1 twinned orientation;

Fig. 6.22: TEM images of the area within the twinned region circled in Fig. 6.21(b) for different diffraction conditions: (a) BF, zone axis $[01-10]$ with $g=[0002]$; (b) DF, zone axis $[01-10]$ with $g=[0002]$ (c-f) BF, zone axis $[1-21-3]$ with (c) $g=[1-101]$, (d) $g=[0-111]$ and (e) $g=[-1010]$; (f) Enlarged area of the red rectangle in (e) to show the shape of the precipitates at both sides of the twin boundary.

Finally, it is very interesting to observe that the β_1' (MgZn_2) precipitates did not elastically rotate with the HCP Mg lattice upon twinning. On the contrary, the rod-like precipitates remained in their original geometrical orientation, so that the original crystallographic orientation relationship with the HCP Mg lattice was completely lost in the twinned region, where the rod-like precipitates are aligned perpendicular to the $\langle c \rangle$ axis. This is clearly seen in Fig. 6.22f showing the β_1' (MgZn_2) precipitates at both sides of the twin boundary at the parent and the twinned regions. Interestingly, no shearing of the β_1' (MgZn_2) precipitates by the basal and pyramidal dislocations was found, in the twins contrary to the case of the parent orientation favourably oriented for basal slip described in section 5.3.4. This must be related to the loss of coherency between precipitates and the HCP lattice upon twinning. Finally, and not surprisingly based on the stress-strain curves, the observations were identical for the $[10\bar{1}0]$ oriented pillars, as shown in Fig. 6.23 and Fig. 6.24.

Fig. 6.23: (a) TEM longitudinal section and corresponding SADP for the (b) parent and (c) twinned orientation for a 7 μm deformed pillar in the peak-aged Mg-2 at.% Zn alloy compressed along the $[10\bar{1}0]$ direction; (d) Misorientation profile across the twin boundary and (e) corresponding t-EBSD map.

The findings are similar to those reported in Y_2O_3 reinforced Mg alloys [161] showing that the Y_2O_3 particles favour the nucleation of several twins as opposed to the nucleation and growth of a single twin, and that the latter favours the activation of pyramidal slip systems [180,181].

Fig. 6.24: TEM images within the twinned region of Fig. 6.23(a) for different diffraction conditions: (a) BF, $g=[0002]$, (b) BF, $g=[0002]$, (c) BF, $g=[-2110]$; (d) $g=[-2110]$.

6.4 Discussion

The results presented above on two micropillar orientations, $[11\bar{2}0]$ and $[10\bar{1}0]$, that were favourably oriented for twinning confirm that the Zn content and its distribution have a strong influence on the process of twin nucleation and growth. Moreover, the results show that a careful characterization of the deformation behaviour is of utmost importance in all cases, because the high anisotropic behaviour of Mg alloys make it difficult to isolate extension twinning from other deformation modes. This is specifically the case for basal slip, especially in those cases where the CRSS for basal slip is very low, like in pure Mg, because basal slip can potentially control the deformation, even if the SF for basal slip is relatively low. This was, for instance, seen in the case of pure Mg oriented

along the $[11\bar{2}0]$ direction (see section 6.3.1), for which plastic deformation was initially accommodated by basal slip, triggering the activation of a kinking deformation mode, instead of twinning. Apart for this, in the rest of the cases studied for Mg-2 at.% Zn in the AQ, RA and PA conditions, the compression behaviour of $[11\bar{2}0]$ and $[10\bar{1}0]$ oriented micropillars was in all cases controlled by the processes of twin nucleation and growth. Fig. 6.25 shows a schematic illustration of the resolved shear stress- engineering strain curves, showing the main stages of deformation for each orientation. In both cases, initial yielding after the first elastic loading was controlled by twin nucleation, followed by a stress drop to a plateau that was controlled by twin growth until the entire micropillar was twinned. After this, the behaviour of $[11\bar{2}0]$ and $[10\bar{1}0]$ oriented micropillars differed, because the first one was controlled by the activation of basal slip in the twinned region at low strain hardening rates, while the second was controlled by the activity of both basal and pyramidal slip, yielding a much higher strain hardening rate.

Fig. 6.25: The schematic illustration of the apparatus performing tests in low load head (load control) or high load head (displacement control). The main stages of deformation for each orientation including twin nucleation and twin growth after twinning along $[10-10]$ direction and $[10-12]$ direction exhibit different strain hardening behaviour.

It should be mentioned that the CRSS for twin nucleation and growth was found to depend on micropillar size and testing apparatus. Regarding size effects, it was found that in most cases, size effects diminished for pillar sizes larger than $5\text{ }\mu\text{m}$, similarly to what was found in the cases of micropillars oriented for basal slip in chapter 5. Therefore, in the following, the results of the $7\text{ }\mu\text{m}$ pillars will be used to estimate values of CRSS for twin nucleation and growth in each case, that are representative of the bulk behaviour.

6.4 Discussion

Regarding the testing apparatus, it should be pointed out that most of the tests were carried out using the low load head of the nanoindentation instrument described in 3.3, which is inherently load controlled, and therefore, the processes of twin nucleation and growth were difficult to distinguish, because this control mode is unable to unload pillars upon twin nucleation, as schematically shown in Fig. 6.25. To solve this issue, additional $7\text{ }\mu\text{m}$ micropillars were milled at different locations of the diffusion couple and tested using the high load head of the same instrument, which is inherently displacement control, in order to obtain representative values of CRSS for twin nucleation and growth, as a function of Zn content for each metallurgical condition. Representative engineering stress-strain curves are plotted in Fig. 6.26 for pure Mg and Mg-2 at.% Zn. The CRSS for twin nucleation and twin growth obtained, using this approach, for each metallurgical condition as a function of Zn content are plotted in Fig. 6.27 (a) and b, respectively.

Fig. 6.26: Representative engineering stress-strain curves for $7\text{ }\mu\text{m}$ micropillars for pure Mg and Mg -2 at.% Zn in AQ, RA and PA condition.

Fig. 6.27: (a) CRSS for twin nucleation for each metallurgical condition as a function of Zn content; (b) CRSS for twin growth for each condition as a function of Zn content; (c) $\Delta CRSS = CRSS_{alloy} - CRSS_{Mg}$, for twin nucleation and (d) $\Delta CRSS = CRSS_{alloy} - CRSS_{Mg}$, for twin growth [75,77,142].

According to Fig. 6.27 the CRSS for twin nucleation is bigger than for twin growth in all cases, except for Mg- 2 at.% Zn in the PA condition. The latter is not surprising considering, as shown in Fig. 6.21, that the β_1' (MgZn₂) precipitates favour the nucleation of several twins in the deformed pillar instead of the nucleation and growth of a single twin. Therefore, the β_1' (MgZn₂) precipitates induce a strong pinning effect on twin boundary migration in Mg-Zn alloys. The strengthening effect of β_1' (MgZn₂) on twin nucleation was estimated from Fig. 6.27 by subtracting the CRSS for pure Mg, to be of the order of ≈ 40 MPa for a Zn content of 2 at.% (Fig. 6.27c), which is slightly lower than the strengthening found for basal slip (≈ 52 MPa) in the previous chapter.

Regarding the effect of Zn content in the solid solution regime (AQ and RA conditions), Fig. 6.27 indicates that the strengthening effect of Zn in the CRSS for twin nucleation and twin growth is similar in the diluted regime and the supersaturated regime. The mechanisms responsible for the strengthening seems to be atomic Zn segregation at the twin boundaries. This is different to the case of basal slip that showed a larger

6.5 Conclusions

strengthening effect of Zn in the supersaturated regime, as summarized in Fig. 5.14. The level of strengthening was also found to be independent of the tendency of Zn to cluster into small Zn rich clusters after long term room temperature aging, as demonstrated in Fig. 6.27d, calculated by subtracting the corresponding CRSS for pure Mg. The strengthening effect of Zn in the solid solution regime on twin nucleation and twin growth was similar and of the order of ≈ 25 MPa for a Zn content of 2 at.%. This is larger than the strengthening effect of Zn in the solid solution regime on basal slip (≈ 6 MPa), in agreement with the preliminary conclusions drawn from instrumented nanoindentation tests in Chapter 4, suggesting that Zn is more effective on strengthening twinning than basal slip.

6.5 Conclusions

The effect of Zn content and its distribution on the CRSS for twinning nucleation and growth in Mg-2 at.% Zn alloys has been evaluated by micropillar compression in the AQ, RA and PA conditions. The key findings can be summarized as follows:

- The strengthening effect of Zn in solid solution in the CRSS for twin nucleation and twin growth is similar in the diluted regime and the supersaturated regime. The mechanism responsible for the strengthening seems to be atomic Zn segregation at the twin boundaries. The strengthening effect of Zn in the solid solution regime was similar for twin nucleation and twin growth and was of the order of ≈ 25 MPa for a Zn content of 2 at.%, larger than the effect of Zn solid solution on the CRSS (≈ 6 -11 MPa, depending on the degree of clustering) for basal slip.
- The β_1' (MgZn₂) precipitates in the PA condition favour the nucleation of several twins in the deformed pillar instead of the nucleation and growth of a single twin. The β_1' (MgZn₂) precipitates induce a strong pinning effect on twin boundary migration in Mg-Zn alloys, presumably because the precipitates lose the coherency with the HCP lattice upon twinning as they do not rotate with the lattice. The strengthening effect of β_1' (MgZn₂) on twin nucleation was estimated to be of the order of ≈ 40 MPa for a Zn content of 2 at.%, which is slightly lower than the strengthening found for basal slip.

Chapter 7

Effect of Zn content on prismatic slip

7.1 Introduction

The results presented so far have shown that Zn alloying has a strong solid solution strengthening effect on basal slip and extension twinning. Moreover, the results demonstrated that the strengthening effect is higher in extension twinning than in basal slip. However, non-basal slip activity is also crucial to improve the ductility and formability of Mg alloys [182–184] and therefore, it is also important to assess the effect of Zn alloying on non-basal slip systems [177,185,186], like prismatic slip, as it might be different to that found on basal slip systems.

As a matter of fact, anisotropic solid-solution hardening in diluted Mg alloys has been widely reported. For instance, Ce and Y have been shown to enhance prismatic slip in Mg-0.2 at. % Ce [191] and Mg-0.5 at.%Y [11], while Al, Li and Y were found to increase pyramidal slip in Mg/Al [10], Mg/Li [192] and Mg/Y [73,84] alloys. With respect to Zn, it has been reported that in the temperature range between -50°C and 25°C, the yield stress of polycrystalline Mg-Zn alloys presents a transition from solid solution softening to hardening at a Zn concentration of 0.6 at. % Zn. This has been attributed to a possible softening of prismatic slip overriding the hardening of basal slip and extension twinning in diluted Mg-Zn alloys [187]. However, direct measurements of the effect of Zn on the CRSS for prismatic slip in Mg-Zn alloys are still lacking.

The high-throughput methodology presented in this work provides a unique opportunity to provide such measurements. However, inducing prismatic slip in micropillar compression experiments in Mg alloys is not straightforward. Ideally, one should compress the Mg single crystal in a direction perpendicular to the c-axis in order to ensure a large SF on prismatic slip systems. However, in this orientation, twinning is always the dominant deformation mode over prismatic slip at room temperature, because the CRSS for prismatic slip is much higher, of the order of 40 MPa in pure Mg [67], than that for extension twinning, 12 MPa [24]. Increasing the testing temperature might be a

7.2 Experimental Procedure

possible strategy to overcome this problem. Twinning is an athermal deformation mechanism, while the CRSS for prismatic slip, a fundamentally lattice resistance controlled process, should strongly depend on temperature [126,127]. Therefore, increasing the testing temperature should suppress extension twinning in favour of prismatic slip when compressing micropillars in the $[11\bar{2}0]$ direction.

Following this idea, the objective of this work was to evaluate the effect of Zn content on the CRSS for prismatic slip on solid-solution strengthened Mg-Zn alloys. For this, and using the diffusion couple approach, *in situ* SEM micropillar compression tests in the temperature range between 25 °C and 100 °C were carried out in grains oriented along the $[11\bar{2}0]$ direction, for Zn contents up to 1 at.% Zn.

7.2 Experimental Procedure

The starting material was the Mg/Mg-2.3 at. % Zn diffusion couple, processed as described in section 3.1, in the as-quenched condition. Microstructure characterization was evaluated by EBSD using the Helios NanoLab 600i microscope equipped with an Oxford-HKL EBSD detector, while the local chemical composition was determined by EPMA, as described in section 3.3.2. Two areas of the diffusion couple were selected for the study. The first, with a composition of 0.5 at.% Zn and orientation of (156.4, 91.8, 4) and the second, with a composition of 1 at.% Zn and orientation of (89, 94.7, 1.2). Both orientations are favorably oriented for twinning and prismatic slip: the SF for prismatic slip and extension twinning were 0.46 and 0.4, at 0.5 at.% Zn, and 0.44 and 0.38 for 1 at. %Zn. respectively.

Square cross-section micropillars were machined by focused ion beam (FEI Helios Nano lab 600i) using the methodology described in section 3.2.3. Side lengths ranging from 5 to 7 μm were selected to minimize potential size effects, based on the previous experience. The micropillar compression tests were carried out *in situ* within the scanning electron microscope at 25 °C and 100 °C at a strain rate of 10^{-3} s^{-1} , using the Hysitron PI87 SEM Picoindenter described in section 3.3. The *in situ* tests allow correcting the misalignment between the flat punch and the top surface of the pillars and tracking their deformation during the test. Slip traces at the surface of the micropillars were carefully examined by high resolution SEM (HR-SEM) in order to determine the active slip systems. To obtain the deformation mechanisms, the deformed micropillars were also longitudinally sectioned and lifted-out for transmission EBSD (t-EBSD) studies, using

the transmission Kikuchi diffraction (TKD) technique. The specimens were thinned to ~ 100 nm thick and finally polished with the ion beam operated at 5 kV by FIB. TKD mapping was carried out in the FEI Helios Nano lab 600i system at 30 kV with a beam current of 2.7 nA and a step size of 10 nm.

7.3 Results and Discussion

7.3.1 Temperature dependent deformation of Mg-0.5 at.% Zn

Representative engineering stress-strain curves for Mg-0.5 at.% Zn micropillars compressed along the $[11\bar{2}0]$ direction at room temperature (RT) and 100°C are shown in Fig. 7.1a and b, respectively. No significant size effects were found for pillar sizes between 5 and 7 μm at RT. The pillars compressed at RT show the same behaviour as that reported for Mg-2 at.% Zn in the same orientation in section 6.3.2. This can be clearly seen in Fig. 7.2, that summarizes the *in situ* observations during the test of one of the 5 μm pillars. After the initial elastic loading, the first strain burst at a strain around 1% occurred at stresses between 55 and 70 MPa. The strain burst indicates the nucleation of an extension twin, as it is expected for Mg in twinning favourable orientations [175], as shown in Fig. 7.2b. The CRSS for twin nucleation was of the order of 35.4 ± 3.2 MPa, in agreement with the results of Fig. 6.27a. The twin grows to consume the entire volume of the pillar and further straining is accomplished by the activation of basal slip in the twinned pillar, as seen in Fig. 7.2c and d.

Fig. 7.1: Representative engineering stress-strain curves for as-quenched Mg-0.5 at.% Zn as a function of pillar size, compressed with loading axis close to $[11\bar{2}0]$, at (a) 25°C and (b) 100°C .

The shape of the stress-strain curves at 100°C was remarkably different, as shown in Fig. 7.1b. First, an anomalous hardening effect with temperature was observed at 100°C . After initial yielding at around 80 MPa, the flow stress showed a strong strain

7.3 Results and Discussion

hardening effect, contrary to the observations at RT. Moreover, the shape of the stress-strain curves was smooth, with no strain bursts that were indicative of twin nucleation at RT. Analysis of the deformed pillar by SEM in Fig. 7.3a indicates the appearance of wavy slip traces, as marked by the green lines. Further analysis of a longitudinal section in the same pillar by t-EBSD in Fig. 7.3b confirmed that no twinning deformation took place at 100 °C, indicating that the slip trace of Fig. 7.3a corresponded to the activation of prismatic slip. Therefore, the anomalous hardening effect observed with temperature seems to be associated with a transition from twinning dominated deformation at RT to prismatic slip controlled deformation at 100 °C. Based on the SF for prismatic slip (0.46) in this orientation, the CRSS for the activation of prismatic slip at 100 °C for Mg-0.5 at.% Zn is estimated to be $\approx 36.8 \pm 1.5$ MPa from the 7 μm pillars, but it should be mentioned that the results at 100 °C seemed to be more affected by size effects than at RT.

Fig. 7.2: (a) Engineering stress-strain curve of a 5 μm micropillar in Mg- 0.5 at.% Zn tested at RT and snapshots taken during the in situ tests corresponding to the marked points in (b) blue, (c) green and (d) yellow.

Fig. 7.3: (a) SEM image of $[11\bar{2}0]$ oriented pillar in Mg-0.5 at.% Zn deformed at 100°C and (b) corresponding *t*-EBSD map in a longitudinal section of the same pillar, confirming that no twinning takes place at 100 °C. The green line marks the appearance of a prismatic slip trace.

7.3.2 Temperature dependent deformation of Mg-1 at.% Zn

Representative engineering stress-strain curves for Mg-1 at.% Zn micropillars along the $[11\bar{2}0]$ orientation at RT and 100 °C are plotted in Fig. 7.4. The behaviour at RT was similar to that found for a lower Zn content, with numerous strain bursts indicative of the activation of extension twinning, but at higher flow stresses, in agreement with what was found in the previous chapter, due to hardening induced by the segregation of Zn solute atoms at the twin boundaries. The results at 100 °C were also consistent with what was found for Mg-0.5 at.% Zn at the same temperature, The stress-strain curves were smooth suggesting the suppression of twinning. A substantial size effect was found between 5 and 7 μm pillars, Taking the 7 μm pillars as reference, the yield stress was somewhat smaller than that found for Mg-0.5 at.% Zn, for the same pillar size.

Analysis of the pillar deformed at 100 °C by *t*-EBSD in Fig. 7.5b confirmed that no twinning deformation took place. The pillars showed a clear indication of the appearance of wavy slip traces, as marked in Fig. 7.5a, that, according to the orientation of the unit cell, corresponded to the activation of prismatic slip. SF for prismatic slip (0.44) in this orientation, the CRSS for the activation of prismatic slip at 100 °C for Mg-1 at.% Zn was estimated to be $\approx 32.34 \pm 1.6$ MPa from the 7 μm pillars.

7.4 Discussion

Fig. 7.4: Representative engineering stress-strain curves for as-quenched Mg-1 at.% Zn as a function of pillar size, compressed with the loading axis close to $[11-20]$, at (a) 25 °C and (b) 100 °C.

Fig. 7.5: a) SEM image of $[11-20]$ oriented pillar in Mg-1 at.% Zn deformed at 100°C and (b) corresponding t-EBSD map on a longitudinal section of the same pillar, confirming that no twinning takes place at 100 °C. The green line marks the appearance of a prismatic slip.

7.4 Discussion

The results indicate that when compressing Mg-Zn micropillars along the $[11\bar{2}0]$ orientation twinning was suppressed in favor of prismatic slip when increasing the temperature from RT to 100 °C. As discussed above, this is, without any doubt, a consequence of the athermal nature of twinning deformation, while the CRSS for prismatic slip, a fundamentally lattice resistance controlled process, should strongly decrease with temperature [126,127]. Therefore, micropillar compression experiments in

this orientation at 100 °C bring the opportunity of studying the effect of Zn alloying on prismatic slip.

Fig. 7.6 summarizes the CRSS determined for prismatic slip in this work as a function of Zn content. Data from literature is also included for comparison purposes. The results are in good agreement with literature data from Akhtar [40], but at somewhat higher stresses, which might be due the fact that the micropillar results seemed to be slightly affected by size effects. Actually, previous studies have suggested that micropillar size might have a significant effect on the competition between prismatic slip and {10-12} tensile twinning when compressing along the a -axis, so the absolute values of CRSS determined should be taken with care. Nevertheless, the rate of change of CRSS with Zn content agrees well with literature data in bulk crystals.

Fig. 7.6: CRSS for prismatic slip at 100 °C determined in this work, together with data from literature at RT and 100 °C [67].

The results confirm that, contrary to what was found for basal slip, Zn alloying induces solid solution softening of prismatic slip. A similar behaviour was also found by Stanford and Barnett [69] in Mg-Zn polycrystals. They found solute softening of prismatic slip in large grains, mainly because cross slip of $\langle a \rangle$ dislocation from basal to prismatic planes is easier than for smaller grains. Some studies suggest that solute-dislocation binding might be one mechanism responsible for solution prismatic softening [188], as the solute-dislocation binding energy of Zn for basal slip is larger than for non-basal slip [70]. However, Akhtar and Teghtsoonian [67] found that solution softening of prismatic slip was quite common in diluted Mg alloys, irrespective of atomic radius ratio,

7.4 Conclusions

changes in the c/a ratio or electron density brought by the solute atoms. Therefore, the most likely mechanism responsible for prismatic softening can be connected with a reduction in the stress required to overcome the Peierls–Nabarro lattice resistance.

On top of the beneficial effect of reducing the plastic anisotropy on the ductility of Mg alloys [70], one important consequence of the strengthening of basal slip and the softening of prismatic slip found with Zn alloying might be the activation of cross-slip from basal to prismatic planes [68]. However, alloying will decrease the stacking fault energy (SFE), increasing the distance between partial dislocations and hindering cross slip between basal and non-basal planes [178,189]. Nevertheless, several observations indicate that cross slip is enhanced. On the one side, the wavy nature of the prismatic slip traces found at 100 °C in Fig. 7.3 and Fig. 7.5 together with the fact that, contrary to basal slip traces, they do not run across the entire cross section of the pillar and seem to vanish within them. On the other side, the strain hardening rate found for prismatic slip in Fig. 7.2 and Fig. 7.4 at 100°C is much higher than for basal slip, as shown in chapter 5. This would also be in agreement with the indentation creep studies presented in chapter 4, demonstrating that cross-slip became the rate controlling deformation mechanism in Mg-Zn alloys at temperatures of 100 °C and above.

7.4 Conclusions

In summary, *in situ* SEM micropillar compression tests along the $[11\bar{2}0]$ orientation at RT and 100°C in Mg-0.5at.% Zn and Mg-1at.% Zn were used to study the effect of Zn alloying on the CRSS for prismatic slip. The following conclusions were obtained:

- Both twinning and prismatic slip are favoured for this loading orientation. At RT, twinning dominates over prismatic slip because the CRSS for prismatic slip is larger than for twinning. However, twinning is suppressed in favour of prismatic slip at 100 °C, presumably because twinning is athermal, while prismatic slip softens with temperature.
- Contrary to the case of basal slip and extension twinning, Zn alloying induces a solid solution softening effect on prismatic slip and facilitates cross-slip of $\langle a \rangle$ dislocations between basal and prismatic planes.

Chapter 8

Main conclusions and future work

8.1 Main Conclusions

The main conclusion of this thesis is that the proposed high-throughput methodology based on the use of diffusion couple together with advanced micromechanical testing constitutes a successful approach, not only for screening purposes, but also to answer fundamental questions on the mechanisms of interaction of solute atoms with the different deformation modes in Mg alloys.

The validation studies carried out in a Mg/Mg Zn diffusion couple as a function of Zn content up to 2 at. % Zn and as a function of the distribution of the Zn atoms in the solid solution and the precipitation conditions, allowed drawing the following additional conclusions:

On the use of nanoindentation to screen strength and creep properties within the diffusion couple:

- Instrumented nanoindentation is unable to provide quantitative estimates of Zn strengthening effects on the different deformation modes of Mg-Zn alloys, because it is not possible to isolate the different deformation modes. Micropillar compression studies are better suited for this. Nevertheless, some interesting conclusions could be drawn.
- The results suggest that Zn solid solution strengthening effects are larger in extension twinning than in basal slip.
- Zn alloying has also a strong effect on creep resistance, especially in the temperature range between RT and 200 °C. The strain rate sensitivity of pure Mg at RT is of the order of 0.025 and the rate controlling mechanism seems to be twin boundary migration, with a creep activation energy of ≈ 80 kJ/mol. Increasing the Zn content

8.1 Main Conclusions

to 0.77 at. % Zn reduces the strain rate sensitivity abruptly, with a transition to a climb controlled dislocation glide regime, with a reduced activation energy.

- At temperatures above 200 °C, the strain rate sensitivity increases and deformation is dominated by basal and prismatic slip, entering a regime in which the rate controlling mechanisms is compatible with cross-slip with an activation energy of ≈ 150 kJ/mol.

On Zn solid solution strengthening of basal slip, prismatic slip and extension twinning:

- The Zn solute atoms are homogeneously dispersed in solid solution in the as-quenched condition, with some tendency to cluster specially for the supersaturated 2 at. % Zn content after room temperature aging for 1000 h.
- Zn clustering and short-range order seems to play an important role on solid solution strengthening of basal slip supersaturated Zn alloys. The strengthening for 2 at.%Zn in the AQ conditions sums up to ≈ 6 MPa for the as-quenched condition, increases to ≈ 11 MPa, with the tendency of Zn to cluster with time. The solid solution strengthening effect is much larger than what is expected for diluted Mg-Zn alloys. Solid solution strengthening is temperature independent between RT and 100 °C and contributes to negligible strain hardening.
- In the case of twinning, the strengthening effect for twin nucleation and twin growth was similar the diluted regime and the supersaturated regime. The mechanism responsible for the strengthening seems to be atomic Zn segregation to the twin boundaries. The strengthening effect of Zn was of the order of ≈ 20 MPa for a Zn content of 2 at. %, larger than the effect of for basal slip.
- Contrary to the case of basal slip and extension twinning, Zn alloying induces a solid solution softening effect on prismatic slip and facilitates cross-slip of $\langle a \rangle$ dislocations between basal and prismatic planes.
- The results show that the solid solution strengthening contributes to reduce the overall anisotropy of Mg-Zn alloys.

On precipitation strengthening of basal slip and extension twinning in Mg-Zn alloys:

- Aging treatments at 200°C for 10 h result in the formation of rod-shape precipitates of $\beta 1'$ (MgZn₂), aligned along the $\langle c \rangle$ axis of the α -Mg matrix, with a mean diameter and length of 11 ± 3 nm and 95 ± 36 nm, respectively.

- A strong strengthening of basal slip by $\beta 1'$ (MgZn_2) precipitates was found. The strengthening for 2 at. % Zn amounts to ≈ 52 MPa at RT, but decreases to ≈ 32 MPa at 100 °C. Precipitation strengthening leads to a large strain hardening due to the increase in forest dislocation hardening induced by the precipitates. The $\beta 1'$ (MgZn_2) precipitates are shearable by the dislocations and order strengthening is expected to be the dominant mechanism responsible for the strong precipitation hardening.
- The $\beta 1'$ (MgZn_2) precipitates favour the nucleation of twins but hinders their growth, because they induce a strong pinning effect on twin boundary migration. This is probably due the fact that the precipitates loss the coherency with the HCP lattice upon twinning of α -Mg. The strengthening effect of $\beta 1'$ (MgZn_2) on twinning was estimated to be of the order of ≈ 40 MPa for a Zn content of 2 at. %, which is slightly lower than the strengthening found for basal slip.
- The results show a much higher strengthening effect than in the solid solution regime, with again an overall reduction in the anisotropy of mechanical properties.

8.2 Future work

The current research has constituted a step forward in the understanding of the deformation mechanisms of Mg alloys and, simultaneously, has opened new avenues for further work that may be pursued in the near future. The following ideas are proposed:

- Evaluation of the effects of Zn and Y on prismatic slip by *in situ* tensile testing at the micro-scale to advance in our understanding of anisotropy and asymmetry of deformation. The strategy followed in this work to suppress twinning in favour of prismatic slip was to increase the testing temperature. A different strategy could be to deform the micrometer scale samples in tension perpendicular to the $\langle c \rangle$ axis, so that extension twinning is suppressed.
- To apply these techniques for multi-component Mg alloys using diffusion multiples, the study should also be extended the precipitation hardened condition to binary, ternary and quaternary alloys. Y [73,84] constitutes an ideal candidate as it significantly reduces the difference between the CRSS of non-basal slip with basal slip and extension twinning.
- To study the effect of grain boundaries on deformation to bridge the gap between the micro and the macro scales. The previous tasks proposed as future work are targeted at studying the single crystal behaviour of Mg alloys, without considering the effect

8.2 Future work

of grain boundary (GB). However, it is well known that GBs have a tremendous effect on the global mechanical behaviour of polycrystalline Mg alloys [23,190,191]. One vital aspect is the transmission of twins across GBs, which is known to depend on the misorientation angle of the adjacent grains.

List of publications

The work in this thesis has been already published or under preparation in the following papers:

- 1) J-Y Wang, **Na Li**, R. Alizadeha, M.A. Monclús, Y.W. Cui, J.M. Molina-Aldareguía, J. LLorca. Effect of solute content and temperature on the deformation mechanisms and critical resolved shear stress in Mg-Al and Mg-Zn alloys. *Acta Materialia*, 170, (2019) 155-165.
- 2) C. Wang, **Na Li**, M.T. Pérez-Pradoa. Effect of solutes on the rate sensitivity in Ti-xAl-yMo-zV and Ti-xAl-yMo-zCr β -Ti alloys. *Scripta Materialia*, 149, (2018) 129-133.
- 3) Na Li, Chuanyun Wang, Yuwen Cui, Lingwei Yang, J.M. Molina-Aldareguía. Fast screening of composition and temperature dependent creep behaviour in Mg-Zn alloys. (in preparation)-chapter 4.
- 4) Na Li, Chuanyun Wang, M.A. Monclús, Torben, J.M. Molina-Aldareguía. Effect of Zn content on basal slip deformation in Mg-Zn alloys. (in preparation)-chapter 5.
- 5) Na Li, Chuanyun Wang, M.A. Monclús, Torben, J.M. Molina-Aldareguía. Effect of Zn content on deformation twinning in Mg-Zn alloys. (in preparation)-chapter 6.
- 6) Na Li, Chuanyun Wang, M.A. Monclús, Torben, J.M. Molina-Aldareguía. Effect of Zn on prismatic slip in Mg-Zn alloys. (in preparation)-chapter 7.
- 7) Na Li, Chuanyun Wang, M.A. Monclús, Dongfeng Shi, Lingwei Yang, J. M. Molina-Aldareguía. The Anisotropic deformation mechanisms of Mg-2Y alloy at RT and high temperature. (in preparation).

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