

Hydride Formation Under Ambient Conditions in HPT-deformed Mg and Mg-Zn-Zr Alloys

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Kurzfassung

Magnesium ist aufgrund seiner hohen theoretischen Wasserstoffspeicherkapazität, seiner hohen Verfügbarkeit und der Reversibilität der Hydridbildung ein vielversprechendes Material zur Festkörper-Wasserstoffspeicherung. Seine praktische Anwendung wird jedoch durch die langsame Kinetik der Hydridbildung eingeschränkt, die häufig auf die träge Dissoziation von Wasserstoff an der Oberfläche und den langsamen Transport durch die MgH_2 -Phase zurückgeführt wird. Es wird vielfach berichtet, dass starke plastische Verformung (severe plastic deformation, SPD) die Hydrierungskinetik von Mg-basierten Materialien verbessert, häufig durch Kornfeinung und die damit verbundene Erhöhung der Korngrenzendichte. Der spezifische Beitrag der Korngrenzen lässt sich jedoch nur schwer von dem Einfluss der gleichzeitigen Änderung der Textur, des Oberflächenzustands und des Nukleationsverhaltens der Hydridphase trennen. In dieser Arbeit wird untersucht, wie SPD-induzierte Defekte, insbesondere Korngrenzen, die Wasserstoffaufnahme und Hydridbildung in reinem Mg sowie in der Mg-Zn-Zr-Legierung ZK60 bei Zimmertemperatur und bei 400 K beeinflussen.

Die Mikrostruktur der Proben wurde durch Hochdrucktordieren (high-pressure torsion, HPT) modifiziert und mittels Elektronenmikroskopie, Positronen-Annihilationsspektroskopie und Röntgendiffraktometrie charakterisiert. Die Wasserstoffaufnahme wurde durch elektrochemische Beladung und Gasphasenbeladung untersucht, unterstützt durch Finite-Elemente-Simulationen der Wasserstoffdiffusion. Zusätzlich wurde für ZK60 in-situ-TEM-Wasserstoffbeladung durchgeführt. HPT führte bei beiden Materialien zu einer starken Verfeinerung des Gefüges und reduzierte die Korngröße von Mg vom Millimeterbereich auf etwa 790 nm und die von ZK60 von etwa $7\text{ }\mu\text{m}$ auf etwa 85 nm. In ZK60 erhöhte HPT außerdem die Versetzungsdichte und veränderte die Verteilung der Zn- und Zr-haltigen intermetallischen Ausscheidungen.

Die elektrochemische Beladung zeigte, dass die Wasserstoffaufnahme bei Zimmertemperatur durch die schnelle Bildung einer MgH_2 -Sperrschicht dominiert wird. Deren Dicke hängt hauptsächlich von der treibenden Kraft für die Nukleation und von der Verfügbarkeit von Nukleationszentren für die Hydridphase ab. Intermetallische Ausscheidungen in ZK60 können als Nukleationsorte für das Hydrid wirken und dazu beitragen, die äquivalente Dicke der Sperrschicht auf etwa 100 nm zu verringern, verglichen mit etwa 200 nm in reinem Mg. HPT führte zu

keiner wesentlichen Änderung dieser Dicke, was darauf hinweist, dass die durch starke plastische Verformung eingebrachten Defekte die Hydridnukleation nicht signifikant fördern. FEM-Simulationen zeigten zudem, dass Effekte der Korngrenzendiffusion mittels elektrochemischer Beladung nicht realistisch beobachtet werden können, da die charakteristische Zeit für die Wasserstoffdiffusion entlang von Korngrenzen in MgH_2 im Vergleich zu den zwischen den Beladungsschritten realisierten Wartezeiten von 30 Minuten zu groß ist.

Im Gegensatz dazu zeigte die Gasphasenbeladung bei Raumtemperatur, bei der Wartezeiten von mehr als 24 h zwischen den Beladungsschritten möglich sind, eine erhöhte Wasserstoffaufnahme nach HPT. Die durch Beladung in der Gasphase erhaltene äquivalente Hydridschichtdicke stieg in Mg von (389 ± 2) nm auf (465 ± 1) nm und in ZK60 von (285.7 ± 0.8) nm auf (471 ± 2) nm. Dies zeigt, dass Korngrenzendiffusion über lange Zeiten relevant wird, wenn die Korngrößen unter etwa $1 \mu\text{m}$ liegen. Dennoch zeigte HPT-ZK60 trotz seiner deutlich feineren Korngröße keine bessere Leistung als HPT-Mg, da die intermetallischen Ausscheidungen einerseits die Mikrostruktur verfeinern, andererseits aber auch die Bildung der Sperrschicht beschleunigen.

Bei 400 K zeigten sowohl die Gasbeladung von Bulk-Proben als auch die in-situ-TEM-Untersuchungen die Bildung von Hydridschichten mit Dicken von bis zu etwa $1.5 \mu\text{m}$ innerhalb weniger Stunden. Unter diesen Bedingungen wurde nach HPT keine signifikante Verbesserung der Hydridschichtdicke oder der Absorptions- und Desorptionszeiten beobachtet. Dies deutet darauf hin, dass Korngrenzendiffusion bei erhöhter Temperatur eine deutlich geringere Rolle spielt, was wahrscheinlich auf die erhöhte Diffusion in der Hydridphase und die thermische Instabilität der durch HPT eingebrachten Defekte zurückzuführen ist.

Insgesamt zeigen die Ergebnisse, dass Korngrenzendiffusion die Wasserstoffaufnahme in Mg-basierten Materialien bei Zimmertemperatur über lange Zeitskalen verbessern kann, während bei moderaten Temperaturen vor allem der Oberflächenzustand und die Hydridnukleation die maßgeblichen Faktoren sind. Die Ergebnisse legen daher nahe, dass sich die zukünftige Optimierung von Mg-basierten Wasserstoffspeichermaterialien weniger auf eine weitere Kornfeinung und stärker auf die Verbesserung der Oberflächeneigenschaften, die Unterdrückung von Oxidation sowie die Optimierung der Geometrien mit großer Oberfläche und kurzen Diffusionswegen konzentrieren sollte.

Abstract

Magnesium is a promising solid-state hydrogen storage material because of its high theoretical hydrogen capacity, abundance, and reversible hydrogenation. However, its practical use is limited by slow hydride formation kinetics, which is often attributed to sluggish hydrogen dissociation at the surface and slow transport through the MgH_2 phase. Severe plastic deformation (SPD) is widely reported to improve hydrogenation kinetics in Mg-based materials, often through grain refinement and the associated increase in grain-boundary density. However, the specific contribution of grain boundaries remains difficult to separate from concurrent changes in texture, surface condition, and hydride nucleation behavior. This thesis investigates how SPD-induced defects, particularly grain boundaries, affect hydrogen absorption and hydride formation in pure Mg and in the Mg-Zn-Zr alloy ZK60 at room temperature and at 400 K.

The samples' microstructure was modified by high-pressure torsion (HPT) and characterized using electron microscopy, positron annihilation spectroscopy and x-ray diffraction. Hydrogen absorption was studied by electrochemical loading and gas-phase loading, supported by finite element diffusion simulations. In situ TEM hydrogen loading was additionally performed for ZK60. HPT strongly refined the microstructure of both materials, reducing the grain size of Mg from the millimeter range to about 790 nm, and of ZK60 from about $7\text{ }\mu\text{m}$ to about 85 nm. In ZK60, HPT also increased the dislocation density and altered the distribution of Zn- and Zr-containing intermetallic precipitates.

Electrochemical loading showed that hydrogen absorption at room temperature is dominated by the rapid formation of a closed MgH_2 layer, which is named blocking layer as it significantly slows the hydrogen absorption kinetics. Its thickness depends mainly on the driving force to nucleation and on the availability of nucleation sites for the hydride phase. Intermetallic precipitates in ZK60 may act as hydride nucleation sites and contribute to reducing the equivalent MgH_2 blocking-layer thickness to about 100 nm, compared with about 200 nm in pure Mg. HPT produced no substantial change in this thickness, indicating that the defects introduced by severe plastic deformation do not significantly promote hydride nucleation. FEM simulations highlighted that it is not realistic to observe grain boundary diffusion effects by electrochemical loading, due to the characteristic time necessary for hydrogen diffusion through grain boundaries in MgH_2 , which is long compared to the 30 min waiting times implemented between loading steps during electrochemical loading.

In contrast, gas-phase loading at room temperature, where waiting times longer than 24 h between loading steps are accessible, revealed enhanced hydrogen absorption after HPT. The equivalent hydride thickness obtained by gas-phase loading increased from (389 ± 2) nm to (465 ± 1) nm in Mg and from (285.7 ± 0.8) nm to (471 ± 2) nm in ZK60, demonstrating that grain-boundary diffusion becomes relevant over long times, when grain sizes fall below about $1\text{ }\mu\text{m}$. Nevertheless, HPT-ZK60 did not outperform HPT-Mg despite its much finer grain size, because intermetallic precipitates both refine the microstructure and accelerate blocking-layer formation.

At 400 K, both bulk gas loading and in situ TEM showed the formation of hydride layers up to about $1.5\text{ }\mu\text{m}$ within a few hours. Under these conditions, no significant improvement in hydride layer thickness or absorption/desorption times was observed after HPT, suggesting that grain-boundary diffusion plays a much smaller role at elevated temperature, likely because of increased hydride-phase diffusion and the thermal instability of HPT-induced defects.

Overall, the results show that grain-boundary diffusion can enhance hydrogen absorption in Mg-based materials at room temperature over long timescales, but that at moderate temperatures the dominant factors are the surface condition and hydride nucleation. These findings therefore suggest that future optimization of Mg-based hydrogen storage materials should focus less on further grain refinement and more on improving surface properties, suppressing oxidation, and designing geometries with high surface area and short diffusion lengths.

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1 Introduction

Magnesium (Mg) is widely recognized as a promising solid-state hydrogen storage material due to its high gravimetric capacity (theoretical 7.6 wt% H in MgH_2), abundance, low cost, and thermodynamically reversible hydrogenation and dehydrogenation processes [1, 2]. The high capacity and reversibility of hydrogenation are related to thermodynamic properties of the magnesium-hydrogen system. However, good thermodynamic conditions are not sufficient to guarantee the applicability of magnesium as a hydrogen storage material; important limitations in technical applications are related to the kinetics of magnesium hydride formation. In particular, the dissociation of hydrogen molecules on magnesium surfaces and the transport of hydrogen in the hydride phase are considered the main causes of slow hydrogenation kinetics. Furthermore, as suggested by Uchida et al. [3], the formation of a continuous MgH_2 “blocking layer” forces hydrogen to diffuse through the hydride phase, which can prevent the complete hydrogenation of bulk materials and often results in them not reaching the theoretical capacity of 7.6 wt% H [4]. Some microstructural factors, such as grain size, defect density, texture, and surface properties, can be modified to improve the kinetics of hydride formation in magnesium. Severe plastic deformation (SPD) techniques can reduce the grain size of magnesium-based alloys, thus overcoming some of the kinetic limitations to magnesium hydride formation [5–8].

Researchers often cite the increased concentration of grain boundaries (GBs) caused by microstructure refinement in SPD as the reason for improved hydrogenation kinetics, since GBs can provide fast diffusion pathways for hydrogen [9–19]. However, grain refinement is not the only effect of SPD techniques on Mg-based materials. SPD introduces a texture that, together with the different resulting surface morphology, can also affect hydrogen absorption in ways that are not always easy to distinguish from the direct effect of hydrogen transport at grain boundaries.

Moreover, most studies regarding hydride formation in magnesium have been conducted at temperatures above 500 K. This temperature range is often chosen because, at 573 K, the hydride phase forms in equilibrium with a H_2 gas pressure of about 1 bar, which is considered a standard pressure for storage applications [2]. A second, more practical, reason for choosing high hydrogenation temperatures is that hydrogen diffusion strongly depends on temperature, leading to faster hydride formation kinetics and minimizing the blocking layer effect when increasing the hydrogenation temperature. As a consequence, magnesium particles in the μm range can be hydrided and dehydrided in reasonable times at temperatures above 500 K. For storage applications

it would however be desirable to hydride and dehydride storage materials at lower temperatures, to increase the overall energy efficiency. For temperatures between 400 and 300 K, experimental results on hydride formation in magnesium are mostly related to thin films, where the short diffusion lengths (usually below 100 nm) allow for relatively fast and complete hydrogenation even with the lower hydrogen diffusivity. These results can however not be directly extended to bulk samples, because of the strong influence of stresses on the equilibrium pressures for hydride formation, as observed among others by Mooij et al. [20] and Wagner et al. [21]. Therefore, in this work, hydride formation was studied for bulk magnesium-alloys at a temperature close to 400 K, to see whether a sufficient hydride volume can be formed in reasonable times in this condition.

Considering again the microstructure formed by SPD, the newly formed defects, particularly grain boundaries and dislocations, are not stable at the temperatures typically used for hydrogen absorption studies [9]. Therefore, to understand the role of grain boundaries in hydride formation, hydrogen absorption has to be studied without heating the samples and possibly destroying the refined microstructure. For this reason, in this work hydrogen absorption was also studied for bulk magnesium and magnesium-alloys at room temperature.

Understanding how different microstructure aspects affect hydrogenation kinetics would allow for an optimized treatment of magnesium for hydrogen storage applications, focusing only on the most influential aspects. Hence, the central motivation of this work is to clarify how SPD-induced microstructures, especially grain boundaries, directly impact hydrogen absorption and hydride formation in Mg and Mg-alloys at moderate temperatures. To achieve this, the effects of transport at grain boundaries must be separated from other effects related to hydrogen dissociation on Mg surfaces, as well as from the factors influencing hydride nucleation and growth.

To tackle these questions, the samples' microstructure is altered by high-pressure torsion (HPT), and characterized by electron microscopy, x-ray diffraction and positron annihilation spectroscopy. The Mg-Zn-Zr alloy ZK60 is studied here in comparison to pure Mg. This alloy was chosen because it reaches a finer microstructure after HPT compared to Mg, and should therefore enhance effects related to H diffusion at grain boundaries. In fact, the alloying elements Zn and Zr play an important role in the dynamic recrystallization process happening during HPT. The intermetallic phases formed by Zn and Zr in Mg can decrease the mobility of grain boundaries, leading to an overall finer microstructure compared to pure magnesium deformed with the same technique. In the field of Mg-based alloys for hydrogen storage modified by SPD, Mg-Zn-Zr and Mg-Al-Zn alloys are often studied. In this work, Mg-Zn-Zr was chosen as it leads to the finest grains after HPT deformation at room temperature. Hydrogen absorption is then studied at two temperatures (room temperature and 400 K) using electrochemical and gas-phase loading, in combination with finite element method (FEM) diffusion simulations. For ZK60, in-situ TEM hydrogen loading is also used to gain insight into the hydride formation process.

This combination of different techniques allows the separation of effects due to surface, texture, grain-boundary diffusion and hydride phase nucleation, and hence establishes which effect is the most relevant in improving hydrogenation kinetics.

This thesis is organized into six chapters. Chapter 2 provides the theoretical background necessary to contextualize the objectives of this work and to interpret the experimental results. It focuses on severe plastic deformation mechanisms, the Mg–H system, and electrochemical hydrogen loading. Chapter 3 describes the experimental techniques employed in this study. It includes sample preparation and characterization by electron microscopy. It also presents the setup and preliminary measurements for electrochemical hydrogen loading, as well as the setup and initial FEM simulations for gas volumetry. The FEM models developed for diffusion simulations are then described, followed by the experimental details of XRD, PAS and in situ TEM hydrogen loading. Chapter 4 presents the experimental results obtained using the above described methods. In particular, the sample microstructure and its modification by HPT are analyzed by means of SEM and XRD. The results of electrochemical hydrogen loading at room temperature are then presented, followed by the FEM simulations of hydrogen diffusion under the same conditions. Next, the gas volumetry results at room temperature and at 400 K are reported. Finally, the results of PAS and in situ TEM hydrogen loading are presented. Chapter 5 discusses and interprets the experimental findings. The discussion addresses the deformation mechanisms active during HPT, the nucleation of magnesium hydride and the formation of the hydride blocking layer, and the influence of microstructure on hydride formation at room temperature and at 400 K. Finally, Chapter 6 summarizes the main findings and presents the conclusions of the thesis.

2 Theoretical Background

As introduced in the previous chapter, magnesium and magnesium-based alloys are of interest as hydrogen storage materials. However, the slow diffusion of hydrogen in magnesium hydride is a limitation to the technical application of magnesium as a storage material. It has been reported in literature that this limitation can be circumvented by refining the material's grain size, as will be discussed in section 2.3.9. A smaller grain size is in fact associated with a higher concentration of grain boundaries, which can act as diffusion pathways for hydrogen, improving the absorption and desorption kinetics. A refined microstructure in metals can be obtained by severe plastic deformation (SPD) techniques, where the grain size is reduced as a result of the large shear strain imposed to the deformed material.

This chapter introduces important theoretical aspects relevant to this work. Section 2.1 introduces basic properties of the studied materials: magnesium and the Mg-Zn-Zr alloy ZK60. Afterwards, section 2.2 presents the methods and mechanisms of severe plastic deformation leading to grain refinement in metals, focusing on materials with hcp crystal structures. Section 2.3 focuses on the magnesium-hydrogen system, discussing thermodynamic and kinetic aspects of hydride formation, as well as the interaction of hydrogen with defects in the crystal structure. Section 2.3 discusses relevant literature regarding hydrogen in SPD-deformed magnesium-alloys. Finally, section 2.4 deals with the theoretical background of electrochemical loading.

2.1 Magnesium and ZK60

Magnesium has a hexagonal close packed (hcp) crystal structure, as shown in Figure 2.1. The crystal lattice belongs to the $P6_3/mmc$ space group and has the following lattice parameters: $a = b = 3.209 \text{ \AA}$ and $c = 5.210 \text{ \AA}$ [22].

In this work the Mg-Zn-Zr alloy ZK60 – containing 6 wt.% Zn and 0.5 wt.% Zr – was employed together with pure magnesium. In terms of atomic percentages, the composition corresponds to 97.6 at.% Mg, 2.3 at.% Zn, and 0.14 at.% Zr. As will be introduced in section 2.2, this particular alloy was chosen in this work because it allows to reach a finer microstructure after HPT compared to pure magnesium. Zirconium acts as a grain refiner, favouring the nucleation

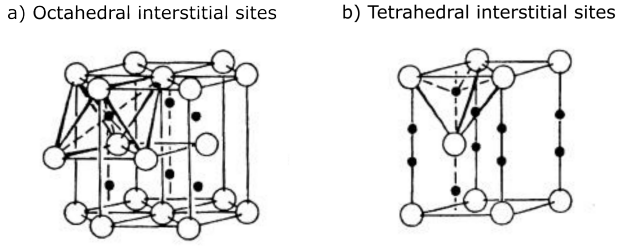


Figure 2.1: Hexagonal close packed (hcp) crystal lattice (white sphere). In panel a) the black spheres indicate octahedral interstitial sites, while in panel b) they indicate tetrahedral interstitial sites. Reproduced with permission from [23].

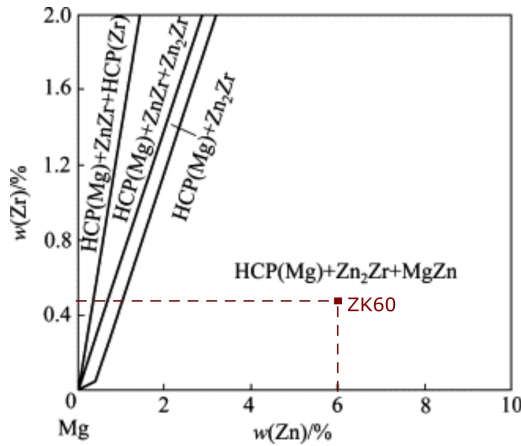
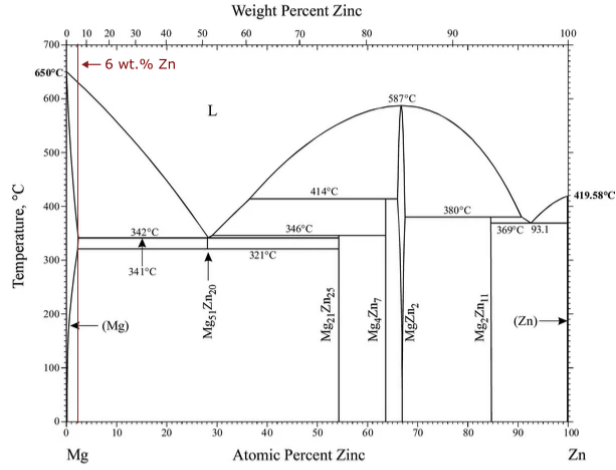


Figure 2.2: Partial phase diagram for the Mg-Zn-Zr system at room temperature. The composition related to ZK60 is highlighted in red. For this composition three phases are expected at equilibrium: hcp Mg, MgZn and Zn_2Zr . Reproduced from [24], available under CC license (<https://creativecommons.org/licenses/by-nc-nd/3.0/>).

of magnesium grains during cooling, which leads to smaller grains after casting compared to pure Mg [27]. Depending on the temperature and on the Zn and Zr concentration, different intermetallic phases can be expected in equilibrium with the hcp magnesium matrix according to the phase diagrams. Figure 2.2 shows the phase diagram for different concentrations of Zn and Zr at 298.15 K in Mg. For the ZK60 composition, Zn_2Zr and MgZn are expected at room temperature in equilibrium with hcp magnesium [24, 28]. Figure 2.3.a shows the binary Mg-Zn phase diagram. At room temperature for 6 wt.% Zn – which corresponds to 2.3 at.% – the equilibrium phase is $\text{Mg}_{21}\text{Zn}_{25}$, which is sometimes also indicated as MgZn. Figure 2.3.b shows the binary phase diagram of Mg-Zr. As can be seen, no intermetallic phases are formed and only a limited solubility of Zr in magnesium is observed. For the Zr content of ZK60 (0.5 wt.% or 0.14 at. %) the solubility of Zr in Mg is negligible at room temperature. In general, the limited

a) Mg-Zn binary phase diagram



b) Mg-Zr binary phase diagram

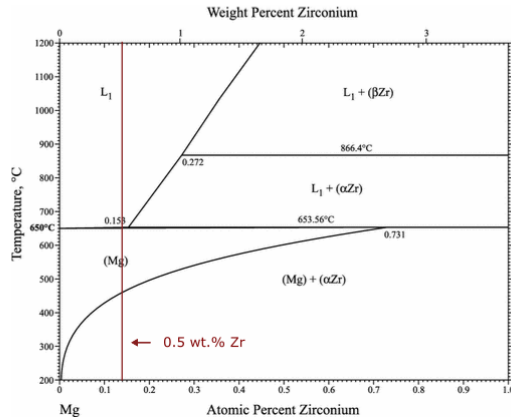


Figure 2.3: Binary phase diagrams for Mg-Zn and Mg-Zr. The red vertical lines show the Zn and Zr concentrations for ZK60. Reproduced with permission from [25, 26]

solubility explains the low Zr content in Mg-Zn-Zr alloys, as higher concentrations would just leads to Zr precipitates in the hcp matrix.

2.1.1 Slip and Twin systems in magnesium

The most relevant systems for dislocation gliding and twinning in magnesium, which will be relevant for the description of plastic deformation mechanisms, are discussed in the following section.

Table 2.1 reports relevant slip systems for magnesium, which are also represented in Figure 2.4. Dislocation gliding in Mg is most commonly observed according to basal slip, which involves the movement of dislocations on the basal (0001) plane. The prevalence of basal slip is explained by its lower critical resolved shear stress (CRSS), as will be explained later in the section. The burger's vector type $\mathbf{a}$ indicates that the burger's vector $\vec{b}$ has the magnitude of the lattice constant a of the hcp crystal, and is oriented along the family of directions $\langle 11\bar{2}0 \rangle$. The prismatic $\langle \mathbf{a} \rangle$ and pyramidal $\langle \mathbf{a} \rangle$ slip systems involve dislocations with a similar burger's vector, which also move along the $\langle 11\bar{2}0 \rangle$ directions, but on different slip planes, namely the prismatic $\{10\bar{1}0\}$ and pyramidal $\{10\bar{1}1\}$ families. Finally, the pyramidal $\langle \mathbf{c}+\mathbf{a} \rangle$ slip system involves a burger's vector that does not lay on the basal plane but on the $\langle 11\bar{2}3 \rangle$ direction, with a magnitude given by $\sqrt{a^2 + c^2}$, and moves on the pyramidal $\{11\bar{2}2\}$ planes in the $\langle 11\bar{2}3 \rangle$ direction [29, 30].

Table 2.1: Common slip systems for Magnesium, including their name, burger's vector type of the moving dislocation, slip direction, slip plane, number of slip systems (total and independent) [29, 30] and critical resolved shear stress (CRSS) [31, 32] at room temperature.

Name	$\vec{b}$ type	Slip direction	Slip plane	n. slip systems		CRSS (MPa)
				total	independent	
basal	$\mathbf{a}$	$\langle 11\bar{2}0 \rangle$	$\{0001\}$	3	2	0.45-0.81 [32]
prismatic $\langle \mathbf{a} \rangle$	$\mathbf{a}$	$\langle 11\bar{2}0 \rangle$	$\{10\bar{1}0\}$	3	2	39 [32]
pyramidal $\langle \mathbf{a} \rangle$	$\mathbf{a}$	$\langle 11\bar{2}0 \rangle$	$\{10\bar{1}1\}$	6	4	48-87 [32]
pyramidal $\langle \mathbf{c}+\mathbf{a} \rangle$	$\mathbf{c}+\mathbf{a}$	$\langle 11\bar{2}3 \rangle$	$\{11\bar{2}2\}$	6	5	86 [31]

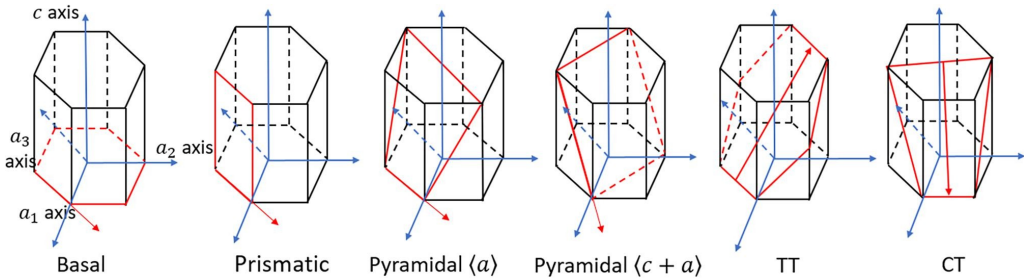


Figure 2.4: Common slip and twin systems for Mg. The slip plane and direction are represented in red. Reproduced from [33], available under creative commons license (<https://creativecommons.org/licenses/by/4.0/>).

Fundamentally, for a slip system to activate, the shear stress applied on the slip plane must be higher than a critical value, known as the critical resolved shear stress (CRSS). CRSS values for pure Mg at room temperature are also reported in Table 2.1. Considering these values, it is obvious why basal slip is the most prominent slip system, having a critical shear stress for activation one order of magnitude lower compared to the other slip systems. However, basal slip only provides two independent slip systems which, according to the Taylor criterion [34], are not sufficient to accommodate an arbitrary plastic deformation in a polycrystalline material. Therefore, to achieve plastic deformation of Mg, some of the other deformation mechanisms with a higher CRSS have to be activated as well. Due to the limited slip systems, twinning also contributes in accommodating plastic deformation of Mg alloys.

In Magnesium, as for other hcp metals, twinning is observed on the $\{10\bar{1}2\}$ plane in the $\langle\bar{1}011\rangle$ direction (indicated as TT in Figure 2.4) [35]. This twinning system is commonly associated to an extension along the c axis – or to a contraction perpendicular to it – and is therefore sometimes referred to as "tension twin" [32]. Alternatively, twinning can be observed in Mg on the $\{10\bar{1}1\}$ plane in the $\langle\bar{1}012\rangle$ [35] as a result of compression along the c axis (CT in Figure 2.4). These twins are therefore referred to as "compression twins" [32]. Similarly to dislocation glide, twinning is also activated above a certain critical resolved shear stress, which is close to 2 GPa for tension twins and between 2.5 GPa and 4.5 GPa for compression twins in Mg at room temperature [32]. Therefore, twinning is much more easily activated compared to prismatic $\langle a \rangle$ (CRSS of 39 GPa) and pyramidal $\langle a \rangle$ (CRSS 48-87 GPa) or $\langle a+c \rangle$ slip (CRSS 86 GPa) as a response to applied stresses.

2.2 Severe Plastic Deformation (SPD) Techniques and Mechanisms

To refine the microstructure of Mg and Mg-based alloys, in this work High-Pressure Torsion, a severe plastic deformation technique, was used. This section introduces some important techniques of severe plastic deformation (SPD), focusing on High-Pressure Torsion (HPT), and their effect on the microstructure of metals.

In general, SPD techniques can create ultra-fine grained or nanostructured materials by applying very large plastic strains. The large plastic strains are accompanied by a high hydrostatic pressure, which prevents the formation of cracks and pores inside the deformed materials. The high hydrostatic pressure also partially prevents the overflow of the deformed material, allowing to maintain its original dimensions after deformation [36]. Research on severe plastic deformation techniques started in the 1940s with the work of Bridgman at Harvard University, which laid the

foundation for the development of High-Pressure Torsion [37–39]. The Equal Channel Angular Pressing (ECAP) technique was developed by Segal in Minsk in the 1980s [40].

2.2.1 High-Pressure Torsion (HPT)

The principle of High-Pressure Torsion (HPT) is illustrated in Figure 2.5. In this method, a thin disc-shaped sample is subjected to very high compressive pressures, while simultaneously being twisted between two anvils. The combined action of pressure and torsion introduces extremely large shear strains, breaking down coarse grains into finer ones. The experimental parameters that can be controlled are the applied pressure P , the number of rotations of the anvils N and their rotation speed. The deformation condition is unconstrained if the material is allowed to flow between the two anvils during torsion (Figure 2.5.a), and constrained if there is no outward flow (Figure 2.5.b). As shown in Figure 2.5, the deformation condition depends on the shape of the anvils: flat anvils which do not apply a lateral pressure on the disc allow for unconstrained deformation. The completely constrained deformation is hard to achieve experimentally, therefore the most common experimental condition is semi-constrained deformation, where a limited outward flow happens between the upper and the lower anvil (Figure 2.5.c) [41].

The introduced shear strain γ depends on N and on the sample geometry according to [42]:

$$\gamma = \frac{2\pi r}{t_d} N \quad (2.1)$$

where t_d is the disc thickness and r is the radial distance from the centre of the sample. The introduced shear strain is therefore zero in the centre of the sample, and increases linearly moving towards the edge, as is visualized in Figure 2.6 for different numbers of rotations. As will be explained in following sections, although the applied strain can increase infinitely with the

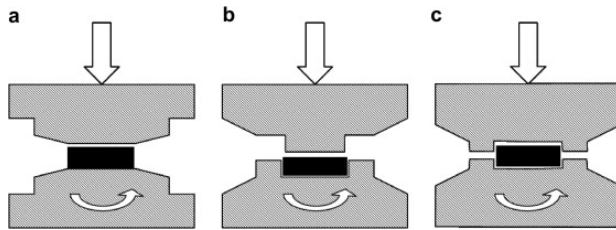


Figure 2.5: Schematic illustration of HPT for (a) unconstrained, (b) constrained and (c) semiconstrained conditions. A disc sample is placed between two anvils, which are rotated while applying a certain hydrostatic pressure. The shape of the anvils controls the outflow of the material during deformation. In the unconstrained condition the material freely flows out of the anvils during deformation, while in the constrained condition outflow is completely prevented. The semiconstrained condition only allows for limited outflow during deformation. From: "Using high-pressure torsion for metal processing: Fundamentals and applications" [41]. Reproduced with permission.

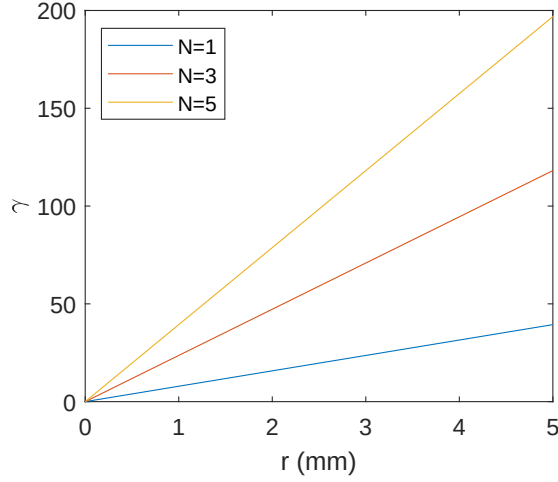


Figure 2.6: Strain introduced by HPT along the radius of a disc according to Eq. 2.1, considering a thickness of $t_d = 0.8$ mm and different numbers of rotations N .

number of rotations, a saturation regime is achieved where further applied shear strain does not affect the resulting microstructure.

2.2.2 Equal Channel Angular Pressing (ECAP)

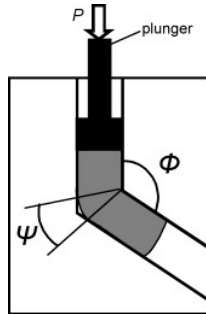


Figure 2.7: Schematic representation of ECAP process: a plunger presses the billet through a die made of two channels with equal cross-section intersecting at an angle ϕ , which imposes intense shear deformation. From: "Severe plastic deformation (SPD) processes for metals" [43]. Reproduced with permission.

The principle of Equal Channel Angular Pressing (ECAP) is illustrated in Figure 2.7. In this process, a billet is pressed through a die consisting of two channels of equal cross-section intersecting at an angle, which imposes intense shear deformation [43]. To press the billet through

the die, pressure is applied through a plunger, often made of hardened tool steel [44]. Repeated passes through the die can produce ultrafine-grained or even nanostructured materials.

The main experimental parameters that affect the outcome of ECAP are [45]:

- Die geometry: defined by the channel intersection angle (Φ) and the outer curvature angle (Ψ), which determine the shear strain imposed per pass.
- Number of passes: determines the accumulated strain and the extent of grain refinement.
- Pressing route: describes the billet rotation between successive passes, affecting texture development and microstructural homogeneity.
- Processing temperature
- Pressing speed/strain rate: impacts dislocation density, flow behavior, and the likelihood of cracking.

The equivalent strain introduced during ECAP can be quantified as [43]:

$$\varepsilon_N = \frac{N}{\sqrt{3}} \left[2 \cot \left(\frac{\Phi}{2} + \frac{\Psi}{2} \right) + \Psi \csc \left(\frac{\Phi}{2} + \frac{\Psi}{2} \right) \right] \quad (2.2)$$

where ε_N is the accumulated strain after N passes, Φ is the channel intersection angle, and Ψ is the outer curvature angle. Similarly to HPT, after a certain number of passes – which depends on the material and on the deformation conditions – a saturation state is reached, where further deformation does not affect the final microstructure. The reason for this behavior is explained in sections 2.2.4 and 2.2.5.

The processing temperature for ECAP results from the tradeoff between grain refinement and cracking. In fact, it has been shown that higher processing temperatures result in coarser microstructures [44] but, at the same time, too low temperatures lead to cracking of the billet, which also prevents further grain refinement [30]. While ECAP at room temperature is possible for some materials, such as Al [44], this deformation temperature is not easily available for magnesium. In the case of magnesium-based alloys, ECAP is usually performed in the 400 - 600 K temperature range [46, 47]. On the contrary, magnesium alloys can be deformed by HPT at room temperature without significant cracking, provided that an adequate pressure is applied. This justifies the choice of HPT as deformation technique for Mg alloys in this work.

2.2.3 Friction Stir Processing (FSP)

Similarly to HPT and ECAP, friction stir processing (FSP) introduces large plastic deformation in metals and can result in a refined microstructure. This technique evolved from the friction stir welding (FSW) process, which is used to join metal plates as shown in Figure 2.8. In FSW, a nonconsumable rotating tool moves in a line between two metal plates, heating and moving the material, and resulting in the formation of a joint in the right conditions. The tool consists of a shoulder moving on the surface, with a pin that penetrates the material's depth. Friction stir processing (FSP) consists in using the FSW tool in Figure 2.8 on a single piece of metal, instead of at the junction between two metal plates [48].

FSP introduces frictional heating and intense plastic deformation, leading to dynamic recrystallization in the stirred zone. As a result, fine and equiaxed recrystallized grains of uniform size can be produced [48]. The obtained microstructure can be varied through the rotation speed, which also affects the frictional heating, and through the applied force. The depth of the stirred zone can be varied through the length of the pin [48].

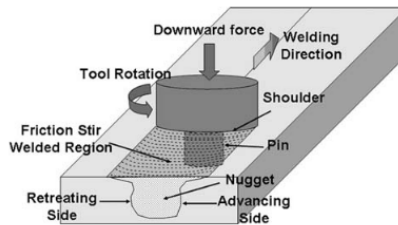


Figure 2.8: Principle of friction stir welding (FSW). A rotating tool with a pin moves between two plates. The developed frictional heat and plastic deformation results in the welding of the two plates. Reproduced with permission from [48].

2.2.4 Grain Refinement Mechanisms during Severe Plastic Deformation of fcc Metals

This section introduces the mechanisms leading to grain refinement during severe plastic deformation of fcc materials.

To start with the most simple and ductile lattice structure, SPD of fcc metals, especially Ni and Cu, has been widely studied [42, 49–53]. The microstructure evolution is described through the Multiplication and Migration of Dislocations (MMDs) model [36], which involves a series of subsequent stages. Initially, dislocations are formed as an effect of severe plastic deformation.

With further deformation, dislocation pile-up occurs within the original grains, leading to the formation of dislocation walls and low-angle grain boundaries (LAGBs) [36, 42, 50, 52]. The misorientation angle then increases with the annihilation of further dislocations by dynamic recrystallization and recovery, leading to high-angle grain boundaries (HAGBs) [36, 42, 50, 52, 54]. The grain refinement continues until an equilibrium between dislocation generation (by plastic deformation) and annihilation (by dynamic recovery, dynamic recrystallization, and grain boundary migration) is reached. This stage is called grain refinement saturation, as further plastic deformation does not affect the resulting microstructure.

An alternative model, introduced by Renk and Pippan [50], identifies the process leading to grain fragmentation mostly with the migration and bulging of grain boundaries and triple junctions, which can be mechanically or thermally induced based on the deformation temperature. This explanation excludes from the deformation mechanism the evolution of LAGBs to HAGBs, which is characteristic of continuous dynamic recrystallization. This alternative process is also known in literature as discontinuous dynamic recrystallization [54]. In discontinuous dynamic recrystallization the mechanism driving the microstructure change is the migration of pre-existing HAGBs, which is in turns driven by the accumulation of dislocations during plastic deformation. The migration of HAGBs can be described through their velocity v , according to [54, 55]:

$$v = m \cdot p_{eff} \quad (2.3)$$

where m is the grain boundary mobility and p_{eff} is the effective pressure driving the grain boundary migration. The effective pressure is proportional to the dislocation density variation across the grain boundary, and it is therefore related to the deformation state of the material [54]. Experimentally, discontinuous dynamic recrystallization is observed above a certain critical strain ϵ_{crit} , which is related to the material and to the deformation temperature. Whether this critical strain is achieved depends again on the competition between dislocation generation by deformation and dislocation annihilation by dynamic recovery [54].

It is still under debate which of the two recrystallization modes – continuous, with the evolution of LAGBs to HAGBs, or discontinuous with the migration of pre-existing HAGBs – is responsible for microstructure changes during severe plastic deformation [50, 54, 56].

The effect of several deformation and material parameters on the saturation grain size has been studied for several fcc metals. In Ni samples, the saturation grain size does not depend on the initial grain size, as similar microstructures are obtained when processing single crystals and nanostructured samples [49, 57, 58]. On the contrary, the deformation temperature and the purity level of the samples play an important role in the achieved microstructure. In particular, a lower deformation temperature and a higher content of impurities or alloying elements can lead to a finer saturation microstructure [42, 49, 50]. The strain rate plays an important role

on the saturation grain size only at elevated deformation temperatures, while its contribution becomes negligible at lower deformation temperatures [50]. The important role of temperature and alloying on the achieved grain size also hints at the importance of grain boundaries migration during SPD, as both factors affect the mobility of grain boundaries.

2.2.5 Grain Refinement Mechanisms during Plastic Deformation of Mg and Mg-alloys

Grain refinement in Mg and Mg-alloys during plastic deformation is usually described in the framework of dynamic recrystallization (DRX), which involves the nucleation and growth of new finer grains in the initial microstructure. Due to the reduced availability of slip systems active at room temperature (see section 2.1.1), the explanation of the process is more complicated than for fcc materials. Different DRX mechanisms have been individuated and linked to the activation of specific glide and twinning systems (see section 2.1.1), mostly on the basis of the deformation temperature and of the sample's microstructure. The most relevant mechanisms are introduced in the following paragraphs.

Continuous Dynamic Recrystallization (CDRX)

Continuous Dynamic Recrystallization (CDRX) consists in the formation of Low Angle Grain Boundaries (LAGBs) by dislocation pile-up, which subsequently evolve in High Angle Grain Boundaries (HAGBs) [54, 59]. For the formation of LAGBs, rearrangement of a dislocations is necessary. This is easier in non-basal planes, which are characterized by a higher stacking fault energy (SFE), and therefore by easier climb and cross-slip of dislocation. For this reason, the activation of non-basal slip is a prerequisite for CDRX [59]. The formation of LAGBs starts in the vicinity of pre-existing grain or twin boundaries, where a local stress field favours the activation of non-basal slip systems (see section 2.1.1). The initial shape of the LAGBs depends on the dominance of basal or non-basal slip. The LAGBs then gradually increase their misorientation by trapping further dislocations. Another prerequisite for this mechanism is the stability of LAGBs, preventing their annihilation by colliding with LAGBs consisting of dislocations with opposite burger's vectors. LAGBs can be stabilized either by the presence of secondary phase precipitates or by sufficiently low temperatures. The increase in misorientation of grain boundaries can also be achieved by the rotation of grains (or of partially recrystallized subgrains), which happens through grain boundary sliding mediated by dislocations [54, 59].

The microstructure resulting from CDRX is characterized by a necklace structure of fine recrystallized grains surrounding the original grain boundaries, and containing coarser grains from the

original microstructure [59]. Therefore, a bimodal grain size distribution might be observed. In the Mg-alloy ZK60, this recrystallization mode has been observed in the temperature range between 470 and 520 K, with evidence of cross-slip of $\mathbf{a}$ dislocations on non-basal planes in the studies of Galiyev et al. [60]. Depending on the initial grain size, the bimodal distribution can be a transient state and later evolve in a uniform distribution, or it can be maintained at saturation, as will be explained in section 2.2.6.

As LAGBs transform into HAGBs, a dynamic equilibrium between emitted dislocations and dislocations trapped by deformation-induced boundaries is reached. Therefore, the transformation of LAGBs into HAGBs provides an effective sink for mobile dislocations. Furthermore, grain boundary sliding can also lead to dislocations absorption. As a consequence, the accumulation of dislocations in the vicinity of the recrystallized regions decreases and the rate of CRDX slows down [59].

Low Temperature Dynamic Recrystallization (LTDRX)

Low Temperature Dynamic Recrystallization (LTDRX) is a type of continuous dynamic recrystallization observed in Mg and Mg-based alloys at temperatures below ~ 470 K. The process is represented schematically in Figure 2.9. The mechanism is similar to that of CDRX, with the difference that the activation of non-basal slip systems is not promoted by the deformation temperature, but by a strong and long-range internal stress field produced by the accumulation of dislocations in the basal plane. The interaction of dislocations moving in non-basal glide systems with dislocation pile-ups in the basal plane leads to the formation of LAGBs, which then evolve in HAGBs by absorbing further dislocations [59]. At low temperatures, HAGBs often show a non-equilibrium structure with strong lattice distortion and accumulation of dislocations in their vicinity [55, 59]. This suggests that at low temperatures recovery does not happen by to absorption of lattice dislocations at HAGBs.

Discontinuous Dynamic Recrystallization (DDRX)

In Discontinuous Dynamic Recrystallization (DDRX), the nucleation of smaller grains happens by bulging of existing grain boundaries, as an effect of strain-induced grain boundaries migration [54], as described in section 2.2.4 for fcc materials. Afterwards, a bridging dislocation wall forms between the bulge and the rest of the parent grain, anchoring the bulged grain boundary. Finally the misorientation of the bridging wall increases by trapping of further dislocations resulting in a new smaller grain surrounded by HAGBs.

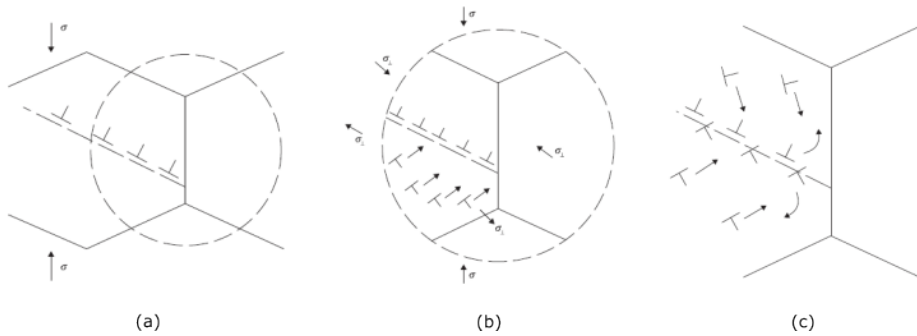


Figure 2.9: Schematic representation of a continuous reaction operating at low temperatures (LTDRX) and resulting in the formation of submicrometer scale grains. (a) The formation of a dislocation pile-ups yielding high long-range stress fields in basal plane. (b) Initiation of $\langle a+c \rangle$ pyramidal slip under high applied and internal stress fields. (c) The formation of a dislocation-induced boundary due to operation of different slip systems within different areas. Reproduced with permission from "Advances in Wrought Magnesium Alloys", 2012, Chapter 5, pag. 199 [59].

The controlling mechanism for the formation of new grains is the climb of non-basal dislocations, which rearrange to form the bridging dislocation wall below the bulged grain boundary. Since dislocation climb involves vacancy diffusion, DDRX becomes relevant at temperatures where diffusion of vacancies in magnesium is sufficiently fast. In the Mg-alloys ZK60, DDRX was observed at temperatures above ~ 620 K by Galiyev et al. [60].

Twinning-associated Dynamic Recrystallization (TDRX)

In Twinning-associated Dynamic Recrystallization (TDRX) the nucleation of the recrystallized grains is associated to the development of twin boundaries. Three nucleation mechanisms have been identified [59]. Firstly, new grains can nucleate by the intersection of primary contraction twins (see section 2.1.1). This mechanism is only observed for coarse grained magnesium with a grain size in the mm range, which can result from casting [61, 62]. In fact, to have the intersection of contraction twins, several twin systems belonging to the $\{10\bar{1}1\}$ family have to be active at the same time, which is facilitated by coarse grains [59]. The second mechanism involves the segmentation of the original grains by twin boundaries, while the third and most likely mechanism involves the subdivision of twin lamellae by LAGBs.

As illustrated here, several mechanisms can be involved in the grain refinement of Mg-based alloys during plastic deformation. The active mechanism depends on the deformation temperature, but also on the initial microstructure of the material. For example, very coarse grains favor the activation of twin-associated DRX. On the contrary, a refined microstructure facilitates $\langle a \rangle$ and $\langle a+c \rangle$ non-basal glide and therefore is more commonly associated to continuous dynamic recrystallization (CDRX) [59, 63]. Also, the presence of second-phase precipitates can

help stabilizing LAGBs, which is a prerequisite for CDRX. During plastic deformation, a combination of different recrystallization modes can be observed at different stages of deformation. For example, in HPT-deformed Mg at room temperature, TDRX is initially observed, followed by continuous reaction according to LTDRX, which can initiate because of the already reduced grain size [16, 64, 65]. Similarly to fcc materials, the contribution of different deformation mechanisms to plastic deformation to grain refinement during SPD is still currently investigated [63]. In particular, the prevalence of continuous or discontinuous dynamic recrystallization is under debate [63].

Regarding the Mg-Zn-Zr alloys (ZK series), which were extensively used in this work, CDRX is often the dominating mechanism. This can result from two aspects. Firstly, Zn and Zr act as grain refiners during the casting and extrusion process [27], leading to a finer grain size before deformation, which favors $\langle a \rangle$ and $\langle a+c \rangle$ non-basal slip. As introduced earlier, this is a prerequisite to observe CDRX or LTDRX. Secondly, intermetallic precipitates as MgZn_2 and Zn_2Zr are present in these alloys and can stabilize LAGBs, which is the second prerequisite for CDRX. This also explains why a finer grain size can be achieved for ZK alloys compared to pure magnesium.

2.2.6 Grain Refinement of Mg and Mg-alloys during ECAP and HPT

The dynamic recrystallization mechanisms introduced in the previous section (2.2.5) are not restricted to severe plastic deformation, as they are valid also at low and moderate strains. Based on the theory of DRX of Mg alloys, and especially on the results of Galiyev et al. [60], Figueiredo and Langdon [66, 67] proposed a model to predict the resulting microstructure of Mg and Mg-alloys processed by ECAP as a function of their initial microstructure and of the processing parameters. Since ECAP is usually performed in the 400 K-600 K temperature range (see section 2.2.2), the main mechanism expected is CDRX (see section 2.2.5), with the nucleation of new smaller grains along grain and twin boundaries, which gradually consume the interior of the original grains. This can lead either to bimodal or to homogeneous microstructures, based on the initial grain size, on the deformation parameters and on the number of passes. The model is illustrated in Figure 2.10. Above a certain critical grain size d_c (Figure 2.10 a, d and g), a bimodal grain size distribution is obtained after the first ECAP pass, as the recrystallized region does not cover the whole area of the original grains. This can evolve in a homogeneous microstructure after several passes, if the size of the recrystallized grains is not too small compared to the initial grain size (Figure 2.10 f and i), otherwise, a bimodal distribution is retained also after several passes as in Figure 2.10.c. Below d_c , a homogeneous microstructure is already achieved after one pass, as illustrated in Figure 2.10.k. Since the grain refinement mechanisms introduced in

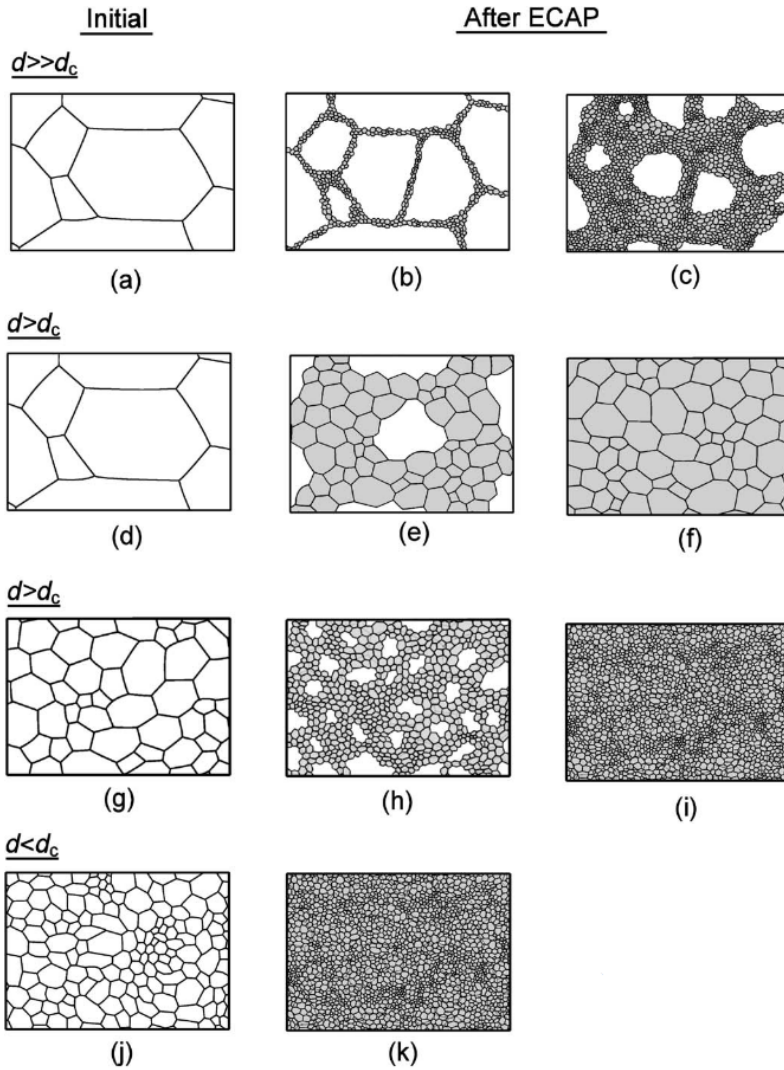


Figure 2.10: A model for the grain refinement of magnesium alloys processed by ECAP: the left column shows the initial condition, the second column shows the structure after one pass and the third column shows the structure after multiple passes; the upper two rows show the same initial structure with different processing parameters and the third and fourth rows show different initial structures. Depending on the initial microstructure and on the number of passes, either a homogeneous microstructure or a bimodal microstructure can result. Reproduced with permission from Figueiredo and Langdon (2010) [66].

the previous section do not depend on the specific deformation method, there is no reason to limit this model to ECAP exclusively. We can therefore extend it to other SPD techniques such as high-pressure torsion (HPT) in a similar temperature range.

In this work, Mg and ZK60 sample were deformed by HPT at room temperature. In this case, the model from Figueiredo and Langdon cannot always be applied to describe the resulting microstructure, as a different recrystallization mechanism is expected to act. In fact, according to LTDRX (see section 2.2.5), the new finer grains do not necessarily nucleate in the vicinity of grain boundaries. For room-temperature HPT deformation, no generalized model has been proposed. Nonetheless, some general considerations can be extended from the reported literature.

Early studies in HPT deformation of Mg and Mg-alloys [64, 65, 68] observed the prevalence of twinning and dislocation pile-ups in the early stages of deformation (strains below $\gamma = 1$), followed by the formation of smaller recrystallized grains without a preferred nucleation site. For comparison, in HPT a strain of $\gamma = 1$ would already be achieved after only 0.04 turns considering a 1 mm thick disc at $r = 4$ mm. With increased strain, the recrystallized areas can increase until they cover the whole volume, or only partially extend leaving a microstructure with a bimodal distribution similar to the one described for ECAP (see Figure 2.10). Later studies also observed twinning at the early stages of HPT deformation [16, 69] and a final bimodal microstructure [16, 42, 69–71]. Since it is not possible to follow in-situ the microstructure evolution during HPT, it is not clear if the bimodal microstructure is caused by the nucleation of recrystallized grains close to grain boundaries according to CDRX (as proposed for ECAP) or by an incomplete recrystallization according to LTDRX.

2.3 Hydrogen in Magnesium

This section introduces relevant aspects of the Mg-H system, which will be necessary to contextualize the objectives of this work and to interpret its experimental results. In particular, the dissociation of hydrogen molecules on the magnesium surface, the phase diagram for H in Mg, the thermodynamics and kinetics of Mg hydride formation and the diffusion of hydrogen in Mg and in grain-boundary rich materials are described. Finally, relevant literature regarding hydrogen absorption in SPD-deformed Mg and Mg alloys is considered.

2.3.1 Hydrogen molecule dissociation on Mg surfaces

The first step in the absorption of hydrogen gas in magnesium is the dissociation and adsorption of the H_2 molecule on the surface of the material. The dissociation of H_2 molecules on

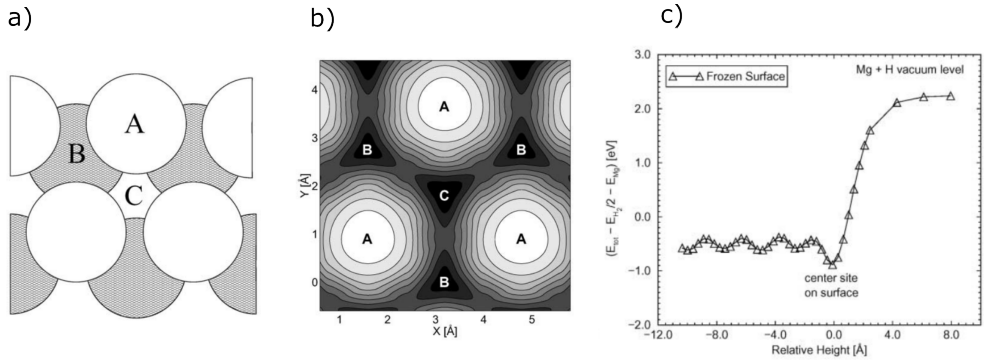


Figure 2.11: a) The (0001) surface of magnesium. Relevant sites are highlighted: A represents a top site, B a hcp site and C a fcc site. b) shows a contour plot of the binding energy of a hydrogen atom on the (0001) surface. The energy minima are at hcp and fcc sites, of which fcc are more stable with a binding energy of -0.88 eV, against the -0.09 eV of hcp sites. c) potential energy curve for a hydrogen atom moving along a set of hcp sites. The energy axis is shifted by the quantity $-(E_{\text{H}_2}/2 + E_{\text{Mg}})$, so that the value zero corresponds to the energy of half a hydrogen molecule not interacting with the magnesium lattice. Reproduced with permission from [73].

magnesium has mostly been studied for the (0001) surface experimentally and through DFT calculations [72–76].

The (0001) surface of magnesium is reported in Figure 2.11.a, while the binding energy of hydrogen atoms on the surface is in Figure 2.11.b. Of the available surface sites, the energy minima correspond to the hcp and fcc sites (B and C in Figure 2.11.b), with a binding energy of respectively -0.09 eV and -0.88 eV [73]. Finally, panel c) shows the energy profile for a hydrogen atom along the fcc sites, compared to the energy of a half hydrogen molecule not interacting with the metal, which corresponds to a energy of zero in the diagram [73]. Therefore, adsorption of a hydrogen atom in the fcc site is energetically favorable compared to a free hydrogen molecule. To achieve this adsorbed state, the hydrogen molecule has to dissociate at the bridge site between two A atoms in Figure 2.11.b, leading to two adsorbed hydrogen atoms, one in the hcp site and one in the fcc site [72, 75, 76]; the atom in the hcp site then diffuses to a neighbor more stable fcc site [72]. Due to this intermediate configuration, the overall dissociation process requires overcoming a potential barrier in the range of 0.75 to 1.15 eV [72, 74–77], which has been measured both experimentally and through DFT calculations. Similarly, a potential barrier of 1 to 1.11 eV has to be overcome during the recombination of a hydrogen molecule from two H atoms adsorbed on the Mg (0001) surface. Limited studies have been performed also on the $(10\bar{1}3)$ Mg surface, resulting in a potential barrier in the same range as the (0001) surface [77]. Due to these large potential barriers, it has been hypothesized that hydrogen dissociation and recombination on magnesium surfaces may be the rate-limiting step in hydrogen absorption and desorption kinetics [75].

In real experimental conditions, clean magnesium surfaces are nearly impossible to encounter. Usually, magnesium is covered by a oxide layer because of its large negative heat of oxidation of -601 kJ/molO [78]. The dissociation barrier of a hydrogen molecule on a magnesium oxide surface has also been studied, and it results to be even larger than for magnesium, in the 2.2 to 2.94 eV range [79–81]. Nonetheless, hydrogen absorption and desorption is observed in oxidized magnesium after activation at elevated temperature. This is attributed either to the cracking of the oxide layer, exposing fresh magnesium surfaces with a lower dissociation barrier, or the activation of the MgO layer [78]. In particular, it has been shown that point defects in the MgO layer can promote the recombination of hydrogen molecules with a low activation energy close to 0.1 eV [78]. Nonetheless, the global desorption rate is slow due to the low concentration of these recombination sites [78].

Given the large dissociation barriers, it is not possible to study hydrogen absorption in magnesium at room temperature. Therefore, in this work magnesium samples have been coated with a palladium capping layer, after removing the already existing oxide layer in UHV (see section 3.1). Unlike for magnesium, the dissociative chemisorption of hydrogen on palladium surfaces does not involve a energy barrier [82, 83] and is therefore effective even at room temperature.

It should be noticed that the problem of hydrogen molecule dissociation is only relevant for gas-phase hydrogen loading of magnesium. As will be introduced in a following chapter (see section 2.4), electrochemical loading directly creates hydrogen atoms on the surface of the loaded metal, bypassing the dissociation step. However, exposing the magnesium surface to electrolytes poses other problems such as corrosion or the formation of magnesium hydroxides in the case of water-containing solutions [84, 85]. Therefore, also the samples used for electrochemical loading were coated with palladium in this work.

2.3.2 Phases and phase diagram of the Mg-H system

Figure 2.12 shows the phase diagram for the Mg-H system at a pressure of $p_{H_2} = 1 \text{ bar}$. At temperatures below $\sim 558 \text{ K}$, two solid phases can exist: the solid solution of hydrogen in magnesium, indicated as (Mg) or also commonly as $\alpha\text{-Mg}$, and the hydride phase MgH_2 . MgH_2 is an intermetallic phase. Above this temperature, the hydride phase is not stable and the hydrogen gas is in equilibrium with a solid solution of H in Mg. The melting temperature of Mg is 922 K, and is not affected by the presence of hydrogen as can be seen in the phase diagram [86]. The highest temperature at which the hydride phase MgH_2 is stable varies strongly with the hydrogen pressure (see section 2.3.4). The maximum solubility of hydrogen in magnesium also varies with the hydrogen pressure and with temperature (see section 2.3.3), but is generally very low with values in the ppm range at RT, so that the hydride phase nucleates already at low hydrogen concentrations.

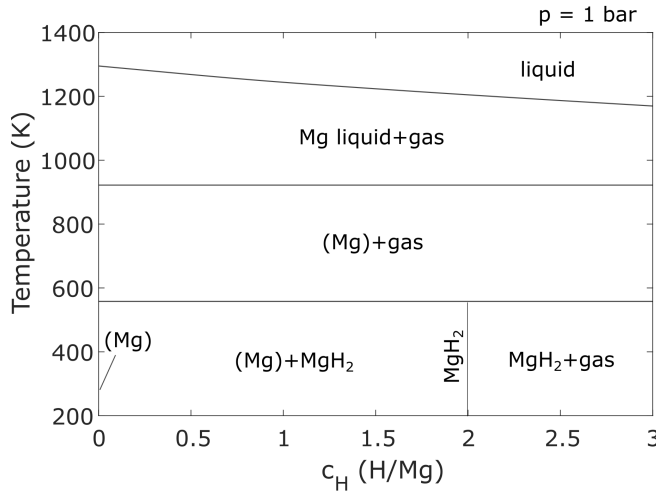


Figure 2.12: Phase diagram of the Mg-H system at a pressure of $p_{H_2} = 1$ bar. The hydride phase MgH_2 is stable at temperatures lower than 558 K. Adapted from [86], under creative commons license (<https://creativecommons.org/licenses/by/3.0/>).

α -Mg has the hexagonal close packed (hcp) crystal structure of Mg, with hydrogen occupying tetrahedral interstitial sites and lattice defects such as vacancies, dislocations and grain boundaries [87]. The hydride phase can have different crystal structures, depending on pressure and temperature, as shown in Figure 2.13. In this work, the relevant hydride phase is α - MgH_2 , since

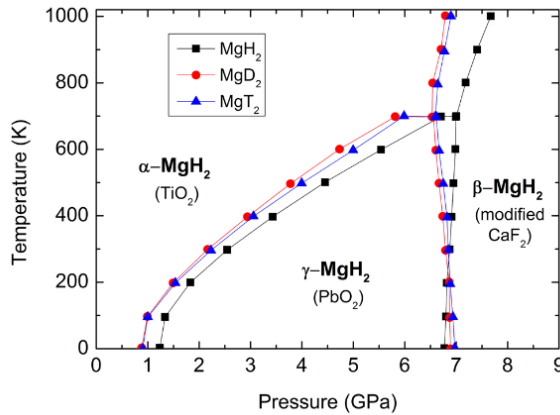


Figure 2.13: Pressure-temperature (P-T) phase diagrams for the three polymorphs of magnesium dihydride for MgH_2 , MgD_2 and MgT_2 . At low pressure the α polymorph shown in Figure 2.14 is expected. Reproduced with permission from [87].

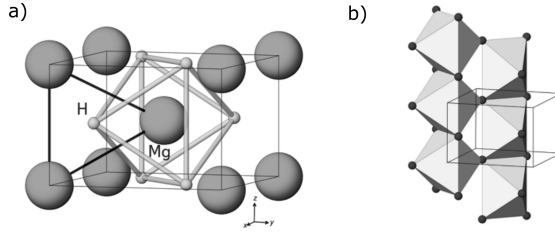


Figure 2.14: a): Crystal structure of α -MgH₂. Each H atom has a coordination number of 3 Mg atoms. Each Mg atom is surrounded by an octahedron of H atoms. b): The MgH₆ octahedra form a chain by connecting their edges. Reproduced with permission from [87].

high pressures were only achieved during severe plastic deformation, which was performed before the introduction of hydrogen in the sample. For all phases, hydride formation is accompanied by a volume expansions of $\sim 30\%$ compared to hcp magnesium [87].

Figure 2.14 shows the crystal structure of the α -MgH₂ phase. The Mg atoms are arranged in a body centered tetragonal lattice, with cell parameters of $a = 4.5025 \text{ \AA}$ and $c = 3.0123 \text{ \AA}$ [88]. The overall crystal structure is similar to that of TiO₂, belonging to the $P4_2/mnm$ space group. Each hydrogen atom is surrounded by three Mg atoms at a distance of $\sim 1.95 \text{ \AA}$ [87]. Magnesium atoms are surrounded by an octahedron with 6 hydrogen atoms at its vertices, with two types of Mg-H bonds: two axial bonds with a distance of $1.948 \text{ \AA}$, and four equatorial bonds with a distance of $1.952 \text{ \AA}$ [87]. The total hydride crystal structure can also be described as a chain of MgH₆ octahedra joined at their edges, as shown in Figure 2.14.b. The bonding between H and Mg atoms has a mostly ionic character, with Mg having a charge of $+1.62e$ and H of $-0.81e$ [87]. Regarding the electronic structure, MgH₂ is an insulator with a band gap of 3 to 5 eV [89]. Hence, hydride formation in Mg causes a metal-insulator transition [90, 91], that can be used to study thermodynamics and kinetics of hydride formation [92].

2.3.3 Hydrogen absorption in hcp Mg

As introduced in the previous section, hydrogen has a limited solubility in hcp Mg, which varies with temperature. The highest values are around 0.02 H/Mg and are observed at temperatures close to the Mg melting point [93]. Stampfer et al. [94] reported the following relationship between the maximum H solubility in α -Mg, indicated as c_H^α , and the temperature T :

$$c_H^\alpha = 107 \cdot \exp\left(-\frac{6225}{T}\right) [H/Mg] \quad (2.4)$$

which was obtained from experimental data in the 700 K-800 K temperature range [94, 95]. The concentration c_H^α indicates the number of hydrogen atoms per Mg atoms (H/Mg). Extending this equation to room temperature, we can expect a very low maximum solubility of $\sim 10^{-7}$ H/Mg.

The absorption of hydrogen at low concentrations in metals is described by Sieverts' law, which gives the relationship between an external hydrogen pressure (p_{H_2}) and the concentration of absorbed atomic hydrogen in a metal (c_H). Sieverts' law is obtained by equating the chemical potential of hydrogen gas molecules to the chemical potential of hydrogen atoms occupying interstitial sites in the metal lattice, resulting in [96]:

$$c_H = \sqrt{\frac{p_{H_2}}{p_0}} \exp\left(-\frac{\Delta H_H^{M-gas} - T\Delta S_H^{M-gas}}{k_B T}\right) \quad (2.5)$$

where $p_0 = 1$ atm, k_B is Boltzmann's constant and ΔH_H^{M-gas} and ΔS_H^{M-gas} are respectively the enthalpy and entropy of solution, while T is the temperature. This expression of Sieverts' law is valid in the context of hydrogen gas (H_2) absorption, and is obtained by writing the chemical potential of hydrogen gas as $\mu_{H_2} = \mu_0 + k_B T \ln(p_{H_2}/p_0)$. In the context of electrochemical hydrogen loading, an equivalent expression of Sieverts' law can be obtained by equating the chemical potential of hydrogen atoms adsorbed at the metal's surface μ_H , to the chemical potential of hydrogen atoms in the metal's interstitial sites, resulting in [97]:

$$\mu_H = \mu_H^{M,0} + RT \ln(c_H) \quad (2.6)$$

in the approximation of low hydrogen concentration, where R is the universal gas constant. Since Sieverts' law only takes into account hydrogen absorption at interstitial sites, significant deviations can be observed when a relevant fraction of hydrogen is located at lattice defects.

2.3.4 Thermodynamics of MgH_2 formation

As introduced in section 2.3.2, at a given hydrogen pressure, the hydride phase MgH_2 is only stable below a certain temperature. Above this temperature, the hydride decomposes and hydrogen is released. In experiments, it is more common to operate at a constant temperature T and with a variable hydrogen pressure p_{H_2} . For a fixed T , there is a threshold hydrogen pressure above which the hydride phase is stable; below this pressure the hydride decomposes. This threshold value is commonly referred to as equilibrium pressure p_{eq} , and is related to temperature according to van't Hoff equation [96]:

$$\ln\left(\frac{p_{eq}}{p_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2.7)$$

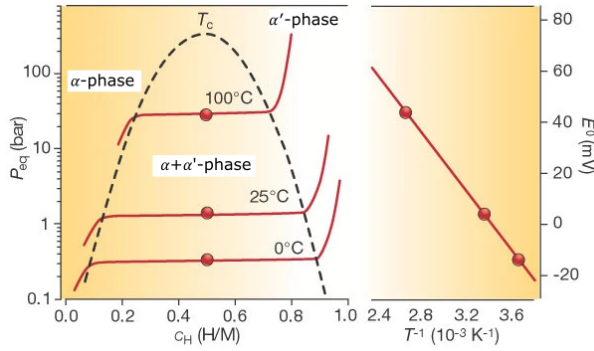


Figure 2.15: Left: Schematic isotherm curves for a general metal-hydrogen system with one solid-solution (α) and one hydride (α') phase. Right: relation between the isotherm plateau pressure and temperature, giving the van't Hoff relation. Adapted with permission from [2].

where ΔH and ΔS are respectively the enthalpy and entropy of decomposition of the hydride phase. Several values have been reported for these quantities [93], generally close to $\Delta H = -74.5 \text{ kJ/mol}$ and $\Delta S = -135 \text{ J/(molK)}$ [94].

The relation between temperature and equilibrium pressure, from which the enthalpy and entropy of formation are derived, can be obtained experimentally by measuring isotherms as shown in Figure 2.15. In p-c-T (pressure-concentration-temperature) isotherms, the temperature of the system is fixed while the hydrogen gas pressure is gradually increased and, at the same time, the concentration of absorbed hydrogen is measured. Alternatively, in the context of electrochemical loading, the hydrogen content in a metal sample is increased, while its surface potential is measured. More details on electrochemical isotherms are reported in section 2.4.2.

As described in the previous sections, at low concentrations hydrogen is absorbed in the metal as a solid solution, and its concentration increases with pressure according to Sieverts' law (see Eq. 2.5). Once the maximum solubility is exceeded, the hydride phase starts forming, in equilibrium with the solid solution phase (see phase diagram in Figure 2.12 for H in Mg). During hydride formation, hydrogen is absorbed in the metal while maintaining a constant pressure. This follows from the equilibrium condition for two or more phases – namely the solid solution, hydrogen gas and hydride phase – which requires a constant chemical potential among them according to Gibbsian thermodynamics [98]. Since, as introduced previously, the chemical potential of hydrogen gas is proportional to the logarithm of its pressure, a constant chemical potential also causes a constant gas pressure during the phase transformation. After the metal to hydride transformation is complete, the hydrogen concentration can further increase only by applying higher hydrogen pressures. Therefore, the boundaries of the pressure plateau in isotherms coincide with the boundaries of the two-phase region at the considered temperature.

Isotherms can be collected either during the formation or the decomposition of the hydride phase. Formation and decomposition isotherms generally show an hysteresis, with higher plateau pressures for hydride formation than for its decomposition. The hysteresis can be caused by several mechanisms. For coherent interfaces between the metal and hydride phases, hysteresis is observed as a result of elastic strain in free open systems, such as a metal in a large hydrogen reservoir at constant pressure and temperature [99]. In this case, the difference between loading and unloading chemical potentials depends on the mechanical properties of the metal and on the concentration difference between the two phases [99]. For thin films, stress can influence the equilibrium chemical potential for hydride formation. In this case, a contribution can come from the interface energy between the hydride and the substrate or the adjacent layers [20, 21, 100, 101]. Moreover, the adhesion to a substrate means that thin films can only expand in the vertical direction, which also leads to stress accumulation upon hydride formation and affects the equilibrium chemical potential [102, 102, 103]. The large elastic stress building during hydride formation can be relaxed by the formation of dislocations [96], creating an incoherent interface. This dissipation of energy also contributes to the hysteresis effects. Moreover, as will be explained in the following section, to drive the phase transformation an overpotential (or underpotential) must be applied. Therefore, depending on the experimental technique, the overpotential necessary to start hydride formation may be measured instead of the true equilibrium pressure or chemical potential. This is often the case for thin films, where the small amount of absorbed hydrogen does not allow to measure pressure drops during gas-phase loading.

The isotherms during decomposition are more often used to determine ΔH and ΔS because they are empirically more consistent across different samples and loading cycles [104]. This may be due to the fact that the loading isotherms are more strongly affected by diffusion and dissociation kinetics, so that the measured loading chemical potential (or pressure) is further from the real equilibrium value. Moreover, stress relaxation during loading may prevent effects related to residual stress in the material.

As shown in Figure 2.15, each isotherm gives one value of p_{eq} . By collecting isotherms at different temperatures, Equation 2.7 can be used to derive ΔH and ΔS .

The van't Hoff plot for MgH_2 formation and decomposition is reported in Figure 2.16, using literature data for bulk (green and purple) and thin film (blue) samples. For bulk samples, data is mostly available for temperatures above ~ 450 K. In this range, the experimental points lay close to each other and are compatible with the introduced values of enthalpy and entropy of decomposition. As expected, equilibrium pressures for hydride formation tend to be higher than for hydride decomposition. Closer to room temperature, the available data is mostly related to thin films. Here, the destabilization of magnesium hydride is attributed to the effect of stress, as previously introduced.

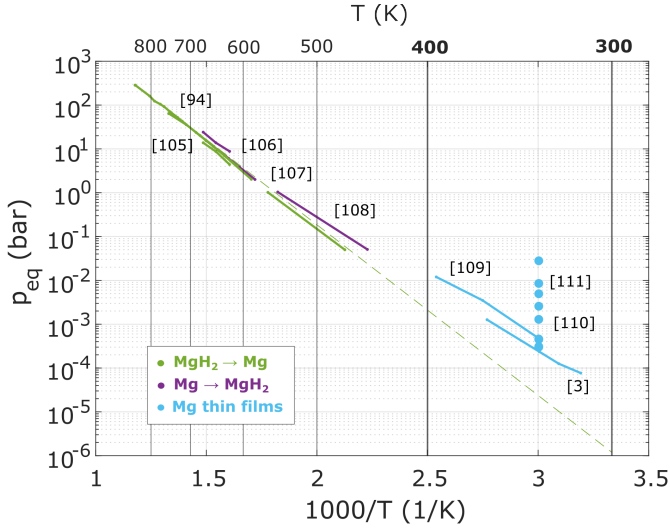


Figure 2.16: Van't Hoff plot based on literature data during hydride formation (purple) and decomposition (green) for bulk Mg [94, 105–108]. Data related to Mg thin films is also reported in light blue [3, 109–111]. The green dashed line gives the equilibrium pressure as a function of temperature according to Eq. 2.7, considering $\Delta H = -74.5 \text{ kJ/mol}$ and $\Delta S = -135 \text{ J/(molK)}$ [94]. The equilibrium pressure for hydride formation/decompositions increases with the temperature. The thin film values deviate from the values reported for bulk Mg. The temperatures studied in this work (300 K and 400 K) are highlighted in bold.

2.3.5 Kinetics of MgH_2 formation

The thermodynamics aspects introduced in the previous section describe the conditions necessary for magnesium hydride to form, which vary based on the pressure and temperature of the system. However, for hydride formation in magnesium, kinetics also play an important role, due to low diffusivity of hydrogen in MgH_2 and to the potentially large barriers to hydride nucleation. Therefore, this section focuses on kinetics aspects of magnesium hydride formation.

The kinetics of the $\text{Mg} \rightarrow \text{MgH}_2$ phase transformation can be described using a classical nucleation and growth model, as proposed by Vigeholm et al. [112] for spherical Mg particles and by Uchida et al. for Mg thin films [3].

In classical nucleation theory, the precipitation of a new phase from a supersaturated matrix is described through the change in Gibbs' free energy ΔG [98]:

$$\Delta G = -V\Delta G_V + A\gamma + V\Delta G_S \quad (2.8)$$

Different aspects contribute to the free energy variation upon nucleation. If the second phase is thermodynamically stable, the total free energy will be reduced by $V\Delta G_V$ after nucleation, where V is the volume occupied by the new phase nucleus. This term is also known as the driving force

to nucleation of the second phase. At the same time, the free energy will be increased by the formation of an interface between the two phases, and by the strain caused by a possible misfit between the matrix and the new phase precipitate. These effects are described respectively by the terms $A\gamma$, where A is the interface area and γ is the interface energy, and $V\Delta G_S$, where ΔG_S is the misfit strain per unit volume. In the case of metal hydrides, the interface free energy density ψ_i for a coherent interface is given by [103]:

$$\psi_i = \frac{1}{2}RT\lambda_c\|\nabla_{cH}\|^2 \quad (2.9)$$

where λ_c is the interface width, T is the temperature, and $\|\nabla_{cH}\|$ is the norm of the gradient of hydrogen concentration across the interface. Therefore, the barrier to hydride nucleation depends on the temperature and on the gradient of hydrogen concentration across the interface. The system's free energy can be further altered by external constraints, introducing an elastic energy term. This effect is particularly relevant for thin films on hard substrates, which can only expand in the vertical direction (perpendicular to the substrate's surface). The elastic free energy density is given by [113]:

$$\psi_e = \frac{1}{2}\epsilon_e\mathbb{C}[\epsilon_e] \quad (2.10)$$

where $\epsilon_e = \epsilon - \epsilon_c - \epsilon_p$ is the elastic strain, obtained by subtracting from the total strain ϵ the plastic strain ϵ_p and the chemical strain ϵ_c caused by the lattice expansion due to hydrogen at interstitial sites; $\mathbb{C}$ is the stiffness tensor for the considered metal. As introduced in the previous section, this term is responsible for the destabilization of the hydride phase in metal thin films [102, 113].

The interplay between the terms with opposite signs in Equation 2.8 determines the critical radius r^* , which is the smallest radius at which a new-phase precipitate is stable, and the nucleation rate $\dot{N}$. The critical nucleus r^* is given by [98]:

$$r^* = \frac{2\gamma}{\Delta G_V - \Delta G_S} \quad (2.11)$$

and the nucleation rate is given by [98]:

$$\dot{N} = N_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (2.12)$$

where ΔG^* is the total free energy variation associated to a radius of r^* , and corresponds to [98]:

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta G_V - \Delta G_S)^2} \quad (2.13)$$

Therefore, a higher driving force to nucleation ΔG_V will lead to a smaller critical radius r^* and to a higher nucleation rate $\dot{N}$.

While the magnitude of the terms γ and ΔG_S are determined only by the characteristics of the two phases, the term ΔG_V depends on the supersaturation of the matrix during the nucleation process [98]. In the case of hydride formation in magnesium, the matrix is α -Mg and the newly formed phase is the hydride MgH_2 . The supersaturation is given by the difference between the introduced H concentration and the maximum solubility of hydrogen in α -Mg at the given temperature. The oversaturation of the alpha phase depends in turn on the loading conditions. During gas loading, as introduced in section 2.3.3, the H concentration in hcp Mg depends on the chemical potential of the hydrogen gas, which increases with the gas pressure. Therefore, a higher loading pressure above the equilibrium value for hydride formation is associated to a higher driving force to hydride nucleation. As a result, we expect a high number of small hydride nuclei when loading with higher pressures. This effect was in fact directly observed in gas loading experiments [4, 112]. In electrochemical loading, the hydrogen concentration is controlled directly by the applied loading current and interval, leading to a similar effect of the driving force on hydride nucleation, as observed by Uchida et al. [3, 114]. Similar effects are also investigated in this work in section 4.3.3.

In the process described so far, homogeneous nucleation was considered. This means that the hydride phase would nucleate at random positions within the Mg matrix. In reality, nucleation is often heterogeneous, meaning that it happens at surfaces, vacancies, dislocations, phase boundaries or grain boundaries. Heterogeneous nucleation is energetically favorable for two reasons. Firstly, when a defect like a grain boundary is removed by the nucleation of a new phase, the overall free energy is further decreased by eliminating the defect energy [98]. Secondly, the stress field associated with defects such as dislocations can decrease the influence of the strain term ΔG_S [98].

In the case of magnesium, hydride nucleation is consistently observed at the sample's surface [4, 112], or at the interface with a capping layer in the case of thin films [114, 115]. Hydride nucleation at grain boundaries, edge dislocations and precipitates has been speculated but not directly observed. Based on this knowledge, Uchida et al. [3] proposed a model for hydride nucleation and growth in magnesium, illustrated in Figure 2.17. In the initial stage (Figure 2.17.a), hydride forms at the film surface in a semi-spherical shape. The distance between hydride nuclei depends on the driving force to nucleation. The hydride nuclei then expand until they connect (Figure 2.17.b), forming a closed hydride layer of thickness L . As will be discussed in detail in the following section, H diffusion in MgH_2 is several orders of magnitude slower than in α -Mg. Therefore, the overall kinetics of hydrogen absorption becomes slower once a closed hydride layer, also called the blocking layer, is formed. From this point on, hydrogen has to diffuse through MgH_2 in order to complete the phase transformation in the remaining magnesium

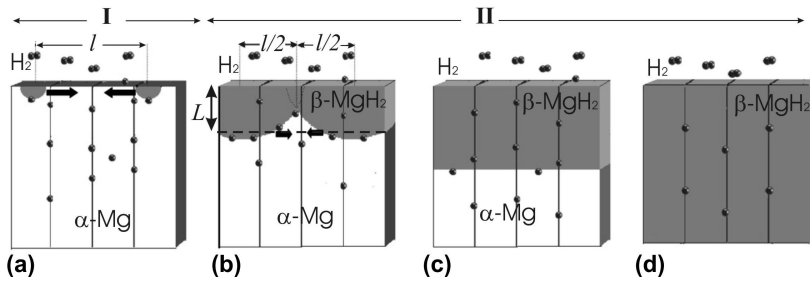


Figure 2.17: Schematic drawing of the hydride nucleation and growth model suggested for the Mg films. (a) The hydride phase ($\beta\text{-MgH}_2$, gray), nucleates at the film surface with a mean distance of l . It grows like half-spheres into the $\alpha\text{-Mg}$ phase (light). Fast diffusion through the $\alpha\text{-Mg}$ phase is possible until neighboring half-spheres meet each other (regime I). (b) Further hydride growth closes the diffusion paths through the $\alpha\text{-Mg}$ phase. A blocking layer of thickness L forms. (c, d) Hydrogen supply is limited by the flux along the grain boundaries and interfaces (regime II). Reproduced with permission from [3].

volume. Since this process is much slower (see following section 2.3.6), a nucleation stage with a low number of hydride nuclei far apart from each other is desirable, as it can delay the blocking layer formation responsible for the reduced hydrogen capacity of Mg samples compared to the theoretical value. This can be achieved by reducing the driving force to nucleation; it was in fact observed experimentally that a lower driving force increases the overall amount of hydrogen absorbed in Mg samples [3, 4, 92, 112]. Alternatively, hydrogen diffusivity through the hydride layer has to be increased. Possible strategies to improve H diffusion will be discussed in the following section.

The introduced model assumes that Mg hydride nucleates and grows as a semi sphere at the film's surface, according to classical nucleation theory. Hamm et al. [115] observed the hydride nucleation and growth in Mg thin films coated with Pd using environmental TEM, and reported a more complex geometry of the hydride precipitates in the early stages of hydride formation. In this case, the growth of the hydride phase was faster across the Mg-Pd interface than in the depth of the Mg sample, leading to an elongated shape of the hydrides. This is explained by the larger availability of H at the Mg-Pd interface compared to the Mg-MgH₂ interface. Nonetheless, even for different shapes of the hydride precipitates during nucleation, a faster diffusion through the hydride layer is desirable to improve the overall hydrogen capacity of magnesium.

2.3.6 Hydrogen Diffusion in Mg and in MgH₂

Hydrogen diffusion in hcp Mg can be described as conventional interstitial diffusion, with hydrogen moving between neighboring tetrahedral sites in the hexagonal lattice. Diffusion coefficients measured experimentally [3, 116, 117] and derived from DFT calculations [75, 118, 119] are reported in Figure 2.18.

Regarding hydrogen diffusion in MgH_2 , several mechanisms have been hypothesized and studied by first-principle DFT calculations. Hydrogen diffusion can be mediated by vacancies [120–123], or it can be related to interstitial hydrogen in the rutile MgH_2 crystal introduced in section 2.3.2 [124, 125]. Both vacancies and interstitial hydrogen can have a neutral, positive or negative electric charge. The neutral state is however not stable [124], therefore positive and negative defects must exist in the same quantities to maintain an overall charge neutrality.

By calculating the energy of formation and of migration of H vacancies and interstitials in different charge states, Park et al. [124] only found slight differences in the diffusion barriers, indicating that there is not one prevalent mechanism in hydrogen diffusion. On the contrary, Hao and Sholl [125] found a prevalence of negatively charged interstitial hydrogen, followed by positively charged vacancies. From the calculated diffusion barriers, a diffusion coefficient for hydrogen in MgH_2 can be obtained. The results from Hao and Sholl [125] are reported in Figure 2.18, together with other literature values. The results from DFT calculations are close to the experimental results of Yao et al. [126], which were obtained from the fitting of hydrogen loading isotherms. Much higher values were reported by Cermak et al. [127] and Stander et al. [128], which were obtained respectively from fitting desorption isotherms of Mg foils and absorption curves of Mg particles. All the studies discussed so far investigated the variations of diffusion coefficients as a function of temperature. Studies conducted at a single temperature are also included in Figure 2.18. At temperatures above 500 K, Stioui et al. [129] reported intermediate values by studying already hydrogenated Mg shaving by NMR, while Bobet et al. [130] obtained similar values from H absorption in Mg powders. At room temperature, diffusion coefficients were measured for Mg thin films. Spatz reported $D_H \sim 10^{-20} \text{ m}^2/\text{s}$ at 305 K [131], which was obtained by fitting the time evolution of hydrogen concentration on the surface of a magnesium thin film loaded from the backside through a Pd-hydride reservoir. The fitting model was derived from Fick's diffusion equation, while the hydride expansion was measured by XPS. Uchida et al. [114] observed a higher value of $D_H \sim 10^{-16} - 10^{-18} \text{ m}^2/\text{s}$ at 300 K by measuring MgH_2 formation with in-situ XRD. A value close to $10^{-17} \text{ m}^2/\text{s}$ was estimated by Hamm et al. [115] by in-situ TEM.

Diffusion in solids is generally described by Fick's first law [98]:

$$J = -D\nabla c \quad (2.14)$$

where J is the flux of the diffusing species, in this case hydrogen, c is its concentration and D is the diffusion coefficient. The diffusion coefficient can be written explicitly as [98]:

$$D = \frac{n}{6} \alpha^2 v \exp\left(-\frac{\Delta G_d}{RT}\right) = D_0 \exp\left(-\frac{\Delta G_d}{RT}\right) \quad (2.15)$$

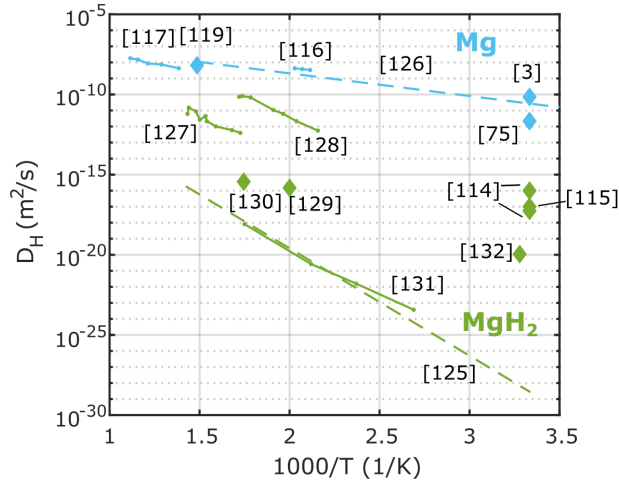


Figure 2.18: Diffusion coefficient of hydrogen in hcp Mg (blue) [3, 75, 116, 117, 119, 132] and in magnesium hydride (green) [114, 115, 125–131] according to different experiments (solid lines) and DFT calculations (dotted lines). The diffusion coefficient is higher for α -Mg compared to magnesium hydride. A large scatter is observed for experimental diffusion coefficients in MgH_2 .

where n is the number of available sites in the vicinity of the diffusing atom, α is the distance between available sites, ν is the mean frequency at which atoms are vibrating about their equilibrium positions, ΔG_d is the energy barrier to diffusion and T is the temperature. This description is based on a classical treatment of diffusion, where atoms can move between positions that are energy minima, such as interstitial sites, by overcoming a potential barrier given by ΔG_d . In the case of interstitial diffusion, ΔG_d only contains the migration barrier. In the case of diffusion mediated by vacancies, ΔG_d also contains the formation energy of the vacancy. The term $n\nu$ describes the frequency of attempts of jumping to the next available site, while the term $\exp(-\Delta G_d/RT)$ describes the probability that such an attempt is successful. The same formula was used by Hao and Sholl [125] to calculate the hydrogen diffusion coefficient from the DFT-calculated value of ΔG_d . This classical treatment of diffusion fails when quantum processes such as tunneling become relevant [133]. Tunneling manifests in Arrhenius plots – such as that in Figure 2.18 – as a non-constant slope in the relation between D_H and $1/T$ [133]. This effect is larger for bcc metals such as V, Nb and Ta, where it can be observed at temperatures lower than $\sim 100\text{ K}$ [133]. However, no tunneling effect has been so far reported for magnesium.

Considering Equation 2.15, the experimental data in Figure 2.18 can be fitted to extract D_0 and ΔG_d . The results of the fit are reported in Table 2.2. The obtained values of ΔG_d are compatible, within experimental errors, to those calculated by DFT [124, 125]. The large difference between values reported in Figure 2.18 at high temperatures are therefore not due to differences in migration and formation energies, which would hint at different diffusion mechanisms. The

Table 2.2: Value of D_0 and ΔG_d obtained by fitting the experimental data in Figure 2.18.

Reference	D_0 (m^2/s)	ΔG_d (eV)
Cermak et al. [127]	$(1.2 \pm 6.6) \cdot 10^{-4}$	(0.98 ± 0.31)
Stander et al. [128]	$(5 \pm 14) \cdot 10^{-2}$	(1.01 ± 0.12)
Yao et al. [126]	$(4 \pm 30) \cdot 10^{-9}$	(1.12 ± 0.28)

calculated values of D_0 are however largely different between the considered references. The value of D_0 depends on the available sites for diffusion n , on the distance between sites α and on the vibration frequency of H atoms in MgH_2 ν . While different diffusion mechanisms would be associated to different values of n and α , this is not enough to explain the difference of several orders of magnitude between the values of D_0 in Table 2.2. To have values of D_0 in the same order of magnitude to those from the work of Cermak et al. [127] and Stander et al. [128], the vibration frequency of H in Mg hydride would have to be in the order of respectively 10^{16} Hz and 10^{18} Hz. However, in the temperature range of these studies, a vibration energy in the order of $k_B T/h \sim 10^{13}$ Hz is expected [118, 134], which is the same value used by Hao and Sholl for their calculation of the diffusion coefficient [125]. These discrepancies could be explained by a systematic error in the fitting of absorption and desorption curves, which introduced a scaling of the measured diffusion coefficients while maintaining the correct dependence on temperature, which is responsible for the consistent slope in the Arrhenius plot (see Figure 2.18).

Nonetheless, Mg thin films show much faster diffusion compared to what is expected for bulk samples. This was explained by Hamm et al. [135] with the hypothesis that hydrogen diffusion in MgH_2 thin films is dominated by grain boundaries, which mostly contribute to the measured diffusion coefficients. More details on hydrogen diffusion in grain boundaries will be discussed in the following section.

2.3.7 Hydrogen interaction with grain boundaries

When absorbed in metals, hydrogen tends to preferentially occupy open volume defect sites, as they generally offer lower energies (larger binding energies) compared to interstitial sites in the defect-free lattice [136]. This is also the case for grain boundaries, which, due to their amorphous structure, can offer a wider range of energy states compared to the single value of interstitial sites. In the framework of statistical mechanics, hydrogen interaction with metals can be described according to Fermi-Dirac statistic with an appropriate partition function $Z(E)$, which describes the density of available energy states at a certain energy E [96]. For this reason, the partition function is sometimes also referred to as density of energy sites (DOSE). The contribution of

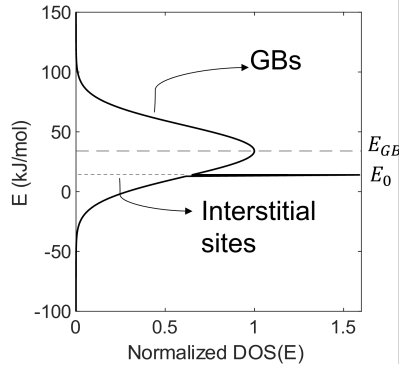


Figure 2.19: DOS(E) from the relation between chemical potential and hydrogen concentration in nanocrystalline 500 nm Mg films from ref. [3] fitted according to the procedure in ref. [97]. The grain boundary energy distribution is represented by a gaussian function, with energy levels above and below those associated to interstitial site, which are represented by a Dirac delta.

grain boundaries to the DOSE can be approximated as a gaussian function [96], while a single value is associated to interstitial sites, according to [97]:

$$DOS(E) = (1 - f)\delta(E - E_0) + \frac{f}{\sigma\sqrt{\pi}} \exp\left(-\frac{(E - E_{GB})^2}{\sigma^2}\right) \quad (2.16)$$

where E_0 is the interstitial site energy, E_{GB} is the mean value of the grain boundary energy, f is the ratio of grain boundaries to interstitial sites and σ gives the width of the grain boundaries energy distribution. This model was first introduced by Kirchheim and Mütschele [137] to explain differences in the isotherms of nanocrystalline Pd compared to bulk Pd at low hydrogen concentrations. More recently, it has been expanded by Wagner and Pundt [97] to include a second type of defects with lower energy states (“deep traps”) as well as stress contributions to the chemical potential, and consistently applied to Pd thin film with different microstructures. We applied a similar model to Mg thin films, allowing to calculate the DOS in Figure 2.19 from the experimental data of Uchida et al. [114] for 500 nm Mg films. Some of the grain boundary energies are below the value for interstitial sites and can therefore act as trapping sites for hydrogen. In nanocrystalline Pd, this is associated to a reduced H diffusivity at low concentrations [137], since the hydrogen atoms in these low energy states must overcome a higher potential barrier to diffusion. This effect vanishes at higher concentration as the filled grain boundaries energy states approach those of interstitial sites. Assuming that grain boundaries retain their physical properties with hydride formation, they should retain their density of states and therefore their diffusivity too. Grain boundaries effects should then emerge again when metal hydrides are formed, due to the lower diffusivity of hydrogen in metal hydrides compared to the solid-solution phase (see Figure 2.18 for H in magnesium).

The interplay between diffusion at grain boundaries and within grains in polycrystalline materials can be described according to Harrison's regimes [138]. In regime A, the diffusing species traverse both grain boundaries and grains at a similar rate, leading to a uniform diffusion front. The effective diffusion coefficient, which can be determined experimentally, depends both on the grain boundary and bulk diffusion coefficients. In regime C, diffusion happens only at grain boundaries, so that the effective diffusion coefficient coincides with the diffusion coefficient at grain boundaries. Regime B represents an intermediate situation, where diffusion happens both along grain boundaries and from grain boundaries towards the interior of grains. The active regime depends on the grain size and on the ratio between the bulk and grain boundaries diffusion coefficients. The relation between Harrison regime and diffusion coefficients was investigated by Hamm et al. [135] by FEM simulations. Regime C is expected when the ratio between the diffusion coefficients of bulk and the grain boundaries is lower than 10^{-3} [135]. Given the low expected bulk diffusion coefficient of H in magnesium hydride at room temperature (see Figure 2.18), Harrison's regime C can be expected for the diffusion of Hydrogen in polycrystalline Mg hydride. In this interpretation, the experimental values for Mg thin films at room temperature – between 10^{-20} and 10^{-16} m²/s [3, 115, 131] – should then coincide with grain boundary diffusion coefficients. Since these values are higher than those expected for bulk MgH₂ ($\sim 10^{-28}$ m²/s), it appears that increasing the density of grain boundaries in Mg sample should improve hydrogen diffusion through the hydride layer. These effects have been experimentally investigated in this work in section 4.5.1 and 4.4.

2.3.8 Hydrogen interaction with dislocations

The interaction of hydrogen with dislocations in metals can be described by the elastic interaction between the stress field generated by a dislocation, and the strain caused by solute hydrogen atoms [96, 139–144]. Generally, it is assumed that the interaction of solute hydrogen with the stress field of dislocations is mainly affected by hydrostatic stresses [96]. Therefore, since screw dislocations do not produce hydrostatic stresses, this effect is commonly studied for edge dislocations. DFT simulations suggest that hydrogen also interacts with the shear stresses produced by screw dislocations, although with a lower binding energy compared to edge dislocations [141, 142, 145]. For simplicity, only hydrogen interaction with edge dislocations is treated in the rest of this section.

The hydrostatic part of the edge dislocation stress field, in a continuum treatment, is given by [96, 139]:

$$p = \frac{Gb(1+\nu)}{3\pi(1-\nu)} \cdot \frac{\sin\theta}{r} \quad (2.17)$$

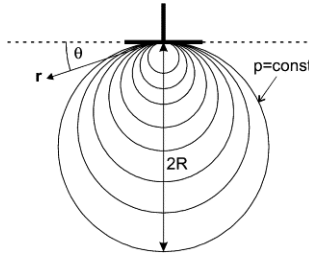


Figure 2.20: Polar coordinates with the origin at the dislocation core, glide plane (dashed line) and circle (cylinder in 3 dimensions) of constant hydrostatic stress. Reproduced with permission from [140].

where θ and r are polar coordinates describing the position relative to the dislocation core (see Figure 2.20), G is the material's shear modulus, ν its Poisson's ratio and b the magnitude of the Burger's vector. A cutoff value for the radius has to be chosen, in order to avoid a non-physical infinite stress value at the dislocation core. Although the shear stress field also interacts with hydrogen [141], its contribution is smaller compared to the hydrostatic stress and will not be treated in this section.

If we consider a cylinder of constant stress below the dislocation line having radius R (see Figure 2.20), the elastic energy due to the interaction of hydrogen with the dislocation is given by [96, 140]:

$$E_{el} = p \cdot V_H = \frac{Gb(1+\nu)}{3\pi(1-\nu)R} \cdot V_H \quad (2.18)$$

where V_H is the partial molar volume of hydrogen in the metal. While V_H depends on the specific material, a typical value for metals is given by $V_H = 2 \times 10^{-6} \text{ m}^3/\text{mol}$ [96].

In the case of hydrogen in palladium, an increased concentration has been observed in the vicinity of edge dislocations by Kirchheim et al. [139] and Maxelon et al. [140]. Considering a cylinder as in Figure 2.20, the increase in H content induced by dislocations, called c_{dist} , is given by [140]:

$$c_{dist} = \delta \rho_d \pi R^2 \quad (2.19)$$

where R is the cylinder radius, ρ_d is the dislocation density, and δ is the fraction of interstitial sites occupied by hydrogen within the cylinder. The value of the radius R depends on the overall hydrogen concentration. Overall, values of R up to $10 \text{ \AA}$ and of $c_{dist} \sim 10^{-2} \text{ H/Pd}$ have been reported for highly deformed Pd samples with a dislocation density of $\rho_d \sim 10^{15} \text{ m}^{-2}$ in the work of Maxelon et al. [140].

Table 2.3: Values of the isotropic shear modulus G , the Poisson ratio ν and the Burger's vector b used to calculate the elastic energy for solute H atoms close to a dislocation in Figure 2.21. For the molar volume, $V_H = 2 \times 10^{-6} \text{ m}^3/\text{mol}$ was used in all cases.

Material	G (GPa)	ν	b (Å)
Pd	44.1	0.39	2.75
Mg	17	0.28	3.21
ZK60	17	0.35	3.21

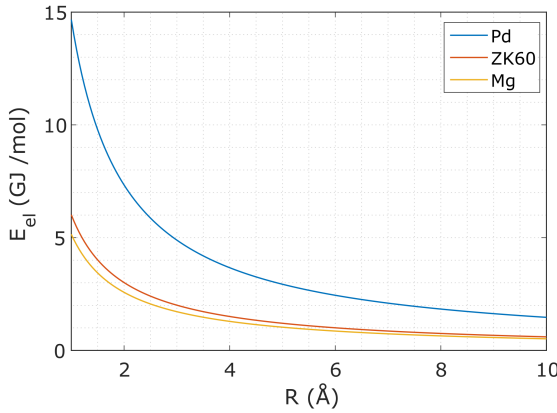


Figure 2.21: Elastic energy describing the interaction between hydrogen atoms and edge dislocations for Pd, Mg and ZK60 calculated according to Equation 2.18 using the values in Table 2.3. The energy is expressed for a cylinder of constant stress with a radius R . The elastic energy is higher for Pd compared to magnesium and ZK60, indicating a higher tendency for hydrogen to segregate at dislocations in Pd.

The interaction of hydrogen with dislocations in Magnesium has not been investigated experimentally so far. Nonetheless, some considerations can be extended using a similar framework to previous studies. The elastic energy describing the interaction between hydrogen and edge dislocations can be estimated using Equation 2.18. Figure 2.21 reports the calculated elastic energy for magnesium and ZK60 compared to palladium. The values used in the calculation are reported in Table 2.3. For the molar volume, $V_H = 2 \times 10^{-6} \text{ m}^3/\text{mol}$ was used. As can be seen in Figure 2.21, the elastic energy is quite close for Mg and ZK60, the only difference being a higher value of ν for the alloy compared to pure Mg. Overall, both curves are lower than the one for palladium but still show a relatively high energy close to the dislocation line. Therefore we deduce that, in magnesium, hydrogen will have a lower tendency to segregate at dislocations compared to palladium, but still some effect might be visible for samples containing a high dislocation density. According to Equation 2.19, the amount of hydrogen segregating at dislocations also depends on the parameter δ , which indicates the fraction of interstitial sites occupied in the high-concentration cylinder. In palladium, it was assumed that the hydrogen concentration

within the cylinder is the same as in the hydride phase, so that $\delta = 0.6 \text{ H/Pd}$ [140]. For magnesium, the value of δ is not known, making it difficult to predict the effect of a certain dislocation density ρ_d on hydrogen absorption.

2.3.9 Hydrogen in SPD Mg and Mg-alloys

Severe plastic deformation (SPD) techniques have been widely used on magnesium-based alloys to refine their microstructure, and have been reported to improve the kinetics of magnesium hydride formation [5–8]. Popular techniques include High-Pressure Torsion (HPT) [9, 16, 18, 146–148], Equal Channel Angular Pressing (ECAP) [9–14, 149, 150] and Friction Stir Processing (FSP) [15, 146, 151]. The working principles of HPT, ECAP and FSP have been introduced respectively in section 2.2.1, 2.2.2 and 2.2.3.

The employed materials are mostly magnesium-based alloys such as Mg-Al-Zn or Mg-Zn-Zr, which allow for a finer microstructure after deformation compared to pure magnesium (see also section 2.2.5). In fact, grains with a diameter of the order of 100 nm can be achieved after HPT deformation of magnesium based alloys [42, 68, 71], while it was shown that the HPT grain refinement of pure magnesium stops at around 1 μm regardless of the deformation parameters [42, 152] and temperature [153], see section 2.2.5. In the reported studies, faster hydrogenation kinetics and larger hydride volumes are observed for the SPD samples compared to their undeformed counterparts. This is attributed to grain boundaries acting as hydrogen diffusion pathways and also to an increased density of other defects such as dislocations and vacancies acting as nucleation sites. There are however some limitations to these studies that need to be considered.

Firstly, in the literature hydrogenation is often studied in conditions associated to an equilibrium pressure of 1 bar for magnesium hydride, meaning that the loading temperature has to be in the 500 K–600 K range (see Figure 2.16). Cengeri et al. [146] argued that grain boundaries are not expected to be stable in this temperature range, especially when cyclic hydrogen loading is considered. They hypothesize instead that the long-term positive influence of HPT and FSP on hydrogen absorption kinetics are related to the formation of vacancy clusters, which are stable at the studied hydrogenation temperature of 623 K and can act as nucleation sites for the hydride phase. Studying hydrogen absorption in magnesium samples at room temperature is complicated because of the low expected equilibrium pressure and diffusion coefficient of hydrogen (see section 2.3.4 and 2.3.6). The issue of low equilibrium pressure can be circumvented by electrochemical loading, as will be explained in the section 2.4.

Secondly, bulk samples produced by severe plastic deformation are further fragmented in order to study hydrogen absorption. This second step can consist in filing [9, 10, 12, 15, 146, 147,

149, 151] or in cold rolling [11, 13, 14]. In the first process, a manual file is used to create small chips from the initial bulk material. In cold rolling, the bulk metal is passed through two or more sets of rolls, reducing its thickness. Both procedures result in magnesium chips with a larger surface-to-volume ratio compared to the initial bulk sample resulting from the SPD process. When performed in a protective atmosphere, they can also open new cracks and surfaces which are not oxidized. Both effects are important to promote hydrogen absorption: a larger surface-to-volume ratio helps contrasting the effect of the magnesium hydride blocking layer, allowing for a larger total hydrided volume, while non-oxidised surfaces promote the dissociation of hydrogen molecules and therefore the absorption of hydrogen in magnesium. In fact, unlike for Pd, magnesium oxide cannot be reduced by hydrogen molecules and is associated to a large barrier to H_2 dissociation (see section 2.3.1). However, this further processing can alter the original microstructure of the SPD samples and can also introduce secondary microstructure effects.

Evidence of this is reported by Silva et al. [151], who compared filings of Mg-Zn-Zr (ZK60) samples in the as-cast state and after FSP. The average grain size in the as-cast state was $150\text{ }\mu\text{m}$, which was reduced to around $1\text{ }\mu\text{m}$ after FSP. They reported different morphologies for the filings related to the different initial microstructures, with thicker chips for the as-cast material and thinner ones for the FSP sample. They also observed a further reduction of the grain size to around 60 nm after the filing process. This may be explained by the further plastic deformation imposed on the metal during the filing process. In the hydrogenation experiment, the thinner chips from FSP samples performed better than the ones from the as-cast material, as can be expected from the higher surface-to-volume ratio. A similar effect was recently reported by Lin et al. [154] for pure Mg and Mg-Li alloys, where the mechanical properties affect the chips morphology and the hydrogen kinetics during the first absorption. A reduction of the grain size after filing to $\sim 80\text{ nm}$ was also reported. A strong effect of the chip morphology, in particular its thickness and serration, on hydrogen absorption kinetics was also observed by Asselli et al. [155] and by Shtuckmeyster et al. [156]. Therefore, filing alters both the morphology and the microstructure of the magnesium chips which are then used for hydrogen absorption studies. The grain size can be further reduced by one order of magnitude when filing after sever plastic deformation, as shown in the study of Silva et al. [151].

Regarding cold rolling, Danaie et al. [157] reported that, in cold rolled samples, magnesium hydride tends to form in the proximity of cracks and of non-metallurgically bonded interfaces (kissing bonds) which are introduced during rolling. Kissing bonds are common following cold rolling, when interfaces separated by a small gap appear to be bonded at large magnifications, but are not actually connected through chemical bonds. Therefore, the specific microstructure created during cold rolling has a direct effect on hydride formation kinetics.

Since the morphology of the chips used for hydrogen absorption/desorption experiments is not always documented, it is difficult to separate direct microstructure effects related to the interaction of hydrogen with grain boundaries from indirect effects related to different chips morphologies. Moreover, the final grain size can be further reduced after filing. When these effects are not considered, the interpretation of hydrogen absorption measurements can be misleading. Fruchart et al. [158] argue that, for Mg powder with a particle size below $1\text{ }\mu\text{m}$, the fast observed hydrogen kinetics depends mostly on the large surface-to-volume ratio. For larger particle sizes, microstructure and texture effects become more relevant.

Regarding texture effects, it was reported by Jorge et al. that the a (0002) texture is associated with a faster absorption kinetics and with an overall larger hydride volume in AZ31 [150] and in pure Mg [159] processed by ECAP and ECAP plus cold rolling. This improvement was attributed to an easier dissociation of H_2 molecules on the (0002) Mg surface, and on the fact that the Mg(0002) direction is advantageous for the formation of $MgH_2(110)$. The orientation relation between magnesium hydride and magnesium has been studied both during hydrogen absorption and desorption [160–163]. The (0002) Mg / (110) MgH_2 orientation relation was observed during hydride decomposition and during hydride formation in (0001) Mg. The prominence of this interface can be explained by its high stability [164], and by the weakening of Mg-H bonds, which promotes the diffusion of hydrogen atoms across the interface [165]. Moreover, Kelekar et al. [161] observed faster hydrogenation kinetics for (110) MgH_2 forming on (0001) Mg, compared to (200) MgH_2 forming on (11 $\bar{2}$ 0) Mg, highlighting the importance of texture during magnesium hydride formation. The films in this study were capped with palladium, therefore excluding effects related to hydrogen dissociation on Mg (see section 2.3.1). Jorge et al. [159] furthermore observed different degrees of oxidation on magnesium surfaces with different orientations, which would also alter the kinetics of hydrogen absorption (see section 2.3.1). The texture effect on hydride formation kinetics is larger in the first loading cycle, where the activation of the oxidized magnesium surface plays a prominent role in the absorption process [159]. Moreover, the initial magnesium orientation is generally not maintained after hydride decomposition [161].

2.4 Electrochemistry aspects relevant to hydrogen loading

In this work, electrochemical reactions were used to study hydride formation in magnesium samples, by measuring electrochemical isotherms. Electrochemical loading can provide more precise information on hydrogen behavior compared to gas-phase loading, which is more often discussed in the literature of metal-hydrogen systems (see section 2.3). This section introduces key electrochemical concepts relevant for interpreting potential–concentration isotherms and highlights

the advantages of this method in terms of richness of information obtained from electrochemical experiments.

Initially, the conditions for electrochemical equilibrium are introduced, focusing on the reactions relevant to this work. Then, two effects that can alter the results of electrochemical loading experiments in this work are introduced, namely the liquid junction potential and the interaction with oxygen in the electrolyte.

2.4.1 Electrochemical Equilibrium and Nernst Equation

2.4.1.1 Conditions for Equilibrium in Chemical Reactions

Considering a generic chemical reaction, the condition for thermodynamic equilibrium is the minimization of the Gibbs free Energy G [98]. In the case of a generic reaction $aA + bB + \dots \leftrightarrow xX + yY + \dots$, where the only variables are the concentrations of reactants and products, the differential of the Gibbs free energy only contains the chemical potentials μ of the different species, and the equilibrium condition can be expressed as [166]:

$$a\mu_A + b\mu_B + \dots = x\mu_X + y\mu_Y + \dots \quad (2.20)$$

The chemical potential of a certain species is in fact defined as the partial derivative of the Gibbs free energy with respect the species' concentration. The chemical potential can be expressed in terms of the activity of the chemical species as [167]:

$$\mu_A = \mu_A^0 + RT \ln(a_A) \quad (2.21)$$

where a_A is the activity of the species A . The activity is related to the concentration of a chemical species and can be generally written as $a_A = \gamma[A]$, where $[A]$ is the molar concentration of the species A [167]. For an ideal solution, the activity coefficient is $\gamma = 1$, so that activity and concentration coincide. For real solutions the activity coefficient γ expresses the deviation from ideal behavior [166].

2.4.1.2 Equilibrium Conditions for Electrochemical Reactions

In the case of electrochemical reactions, the transformation of the reactants in products involves the exchange of one or more electrons and is driven by the presence of a potential difference. These reactions are mediated by electrodes, which supply the necessary electrons; the electrodes are commonly metals immersed in a solution containing ionic species. The equilibrium condition

for an electrochemical reaction must therefore be extended from the one in Eq. 2.20, to account for the electric potential of the involved species. This is done by adding a term describing the electric potential to the chemical potential μ , obtaining the electrochemical potential $\bar{\mu}$ [166]:

$$\bar{\mu}_A = \mu_A + ZF\phi \quad (2.22)$$

where μ_A is the chemical potential according to Eq. 2.21, Z is the electric charge number, ϕ is the electric potential, and F is the Faraday's constant, which corresponds to the electric charge of one mole of electrons. The equilibrium condition for electrochemical reactions is then obtained by equating the electrochemical potentials of reactants and products, and is known as the Nernst Equation. According to the definition of the electrochemical potential, the Nernst equation also contains the potential difference between the electrode (ϕ_M) and the solution (ϕ_S), which is commonly indicated as the electrode potential $E = \phi_M - \phi_S$. An example of the Nernst equation relevant to the studied system is given in the following paragraph.

2.4.1.3 Equilibrium Condition for H loading in Metals

In this work, electrochemical reactions are employed to load atomic H in Pd-coated Mg samples, using 6M KOH as an electrolyte. This electrolyte was chosen because his alkaline pH of 14.778 prevents the corrosion of magnesium in water-based solutions; more details on this aspect are given in section 3.4. Moreover, as will be illustrated in this section, the high concentration of OH^- ions in the electrolyte stabilizes the measured electrode potentials.

The relevant electrochemical reaction during H electrochemical loading in KOH is [137, 168]:



Therefore, KOH is not directly involved in the loading reaction, but it serves to stabilize the measured potentials, as will be explained later in this section. Hydrogen adsorption results from the splitting of a water molecule, mediated by one electron at the sample's surface. Following the water splitting, one H atom is adsorbed at the surface and one OH^- molecule is solved in the electrolyte. Equating the electrochemical potential of H_2O and e^- to that of H_{ads} and OH^- , we obtain the following Nernst Equation describing the equilibrium condition:

$$E = E_0 - \frac{RT}{F} \ln \left(\frac{a_{OH^-}}{a_{H_2O}} \right) - \frac{\mu_H}{F} \quad (2.24)$$

where the electrode potential E is the difference between the electric potential in the metal sample and in the KOH solution, the logarithmic term accounts for the chemical potentials of H_2O and

OH^- according to Eq. 2.21, E_0 accounts for all the constant terms and μ_H describes the chemical potential of the adsorbed hydrogen atoms.

The Nernst equation for this system implies that, in electrochemical equilibrium conditions, the electrode potential of the metal sample is proportional to the chemical potential of hydrogen adsorbed on the metal surface. Therefore, during electrochemical hydrogen loading we can measure the sample's equilibrium potential and directly gain information on the chemical potential of hydrogen in the system. After surface adsorption, the H atoms diffuse in the subsurface and bulk of the metal, where eventually the hydride phase is formed (see Figure 2.11). In thermodynamic equilibrium conditions, the hydrogen chemical potential is equal in all phases present in the system, which include surface states, solid solution and eventually the hydride phase. Therefore, we can use the surface potential to study not only hydrogen adsorption but also hydride formation in bulk metallic samples.

The direct proportionality between surface potential E and H chemical potential μ_H further assumes that the activity of OH^- and H_2O is not strongly influenced by the loading reaction, so that it can also be treated as a constant term. This condition is in general true for water molecules in an aqueous solutions since their initial concentration is very high and the extra molecules introduced following the reaction in Eq. 2.23 would only introduce a small variation in the activity, which does not strongly affect the resulting potential. Regarding OH^- ions, whether their activity is strongly affected by the H loading reaction depends on their initial concentration, on the amount of OH^- molecules introduced for each loading step and on the total volume of the electrolyte. In the following, the effect of OH^- activity is quantified for the case relevant to this work.

In this work, 6M KOH was used in a cell with a 100 mL volume. For each loading step, the amount of OH^- created is $n_{OH^-} = 3.7 \times 10^{-8}$ mol (for details see section 3.4). The initial concentration of OH^- in 6M KOH is 6 M, since KOH completely dissociates in K^+ and OH^- in water. The concentration change for OH^- following one loading step would be 3.7×10^{-7} M; the associated potential change, calculated through Eq. 2.24, is $\sim 1.6 \times 10^{-9}$ V at room temperature, which is much smaller than potential variations measured during hydrogen loading (see paragraph 4.3.2). Therefore, we can consider the logarithmic term in Eq. 2.24 as a constant and attribute the measured variations in the electrode potential exclusively to hydrogen effects. Therefore, even though the reaction driving hydrogen loading in metal electrodes only involves the splitting of water molecules (see equation 2.23), a high concentration of OH^- ions is necessary to obtain stable potentials which are only related to the hydrogen content in the metal electrode. This is achieved through aqueous solutions with a high concentration of KOH, such as 6M in this work.

To summarize, when thermodynamic equilibrium is achieved, the surface potential of a metal electrode loaded with H in KOH is directly proportional to the chemical potential of hydrogen in the metal. By recording the evolution of the equilibrium surface potential with hydrogen concentration, we can therefore study hydrogen absorption and hydride formation in metallic samples.

2.4.2 Electrochemical isotherms

In isotherms, a term proportional to the hydrogen chemical potential is plotted as a function of the hydrogen content in the sample (see also section 2.3.4) [96]. As introduced in the previous paragraph, the metal surface potential, in equilibrium conditions and with the appropriate electrolyte, is proportional to the hydrogen chemical potential and can be therefore used to build the isotherm y-axis. When hydrogen loading happens through electrochemical reactions, the hydrogen content in moles (n_H) can be estimated using Faraday's law [169]:

$$n_H = \frac{I\Delta t}{F} \quad (2.25)$$

where I is the current intensity and Δt the current duration. Therefore, electrochemical isotherms can be measured by stepwise electrochemical hydrogen loading. First, a current is applied for a certain time interval. Then, after hydrogen absorption the surface potential is measured in equilibrium conditions, so that it represents the chemical potential of hydrogen in the sample.

2.4.3 Liquid Junction Potential

A second phenomenon that affects the measured equilibrium potential is the liquid junction potential. A liquid junction potential occurs when two solutions with different concentrations of ionic species are in contact, for example when the internal solution of a reference electrode does not match the external solution. This phenomenon is relevant to this work because a reference electrode filled with 1M KOH was used to measure potentials in a 6M KOH electrolyte (see section 3.4). This causes a shift in the measured potential, which has to be corrected when evaluating experimental potentials, as explained in section 3.4.

Besides having two different concentrations of ionic species, the second condition for the formation of a liquid junction potential is that ions with opposite electrical charge also have different diffusion coefficients in the electrolyte, as is the case for K^+ and OH^- ions in KOH. When the two solutions are put in contact, all ions diffuse against the concentration gradient. However, since a species of ions is faster than the other, their concentration changes faster along the liquid-liquid interface. This leads to the formation of an electric potential, which acts in the opposite

direction with respect to the concentration gradient for the fast species (and in the same direction for the slow species). As a consequence, a potential difference is maintained at the liquid-liquid interface once the steady state is reached [166].

The conditions to develop a liquid junction potential are met for KOH aqueous solutions with different concentrations, because of the higher diffusion coefficient of OH^- ions compared to K^+ ions. At 298.15 K, the diffusion coefficient for OH^- in aqueous solutions is in fact $D_{OH^-} = 5.27 \times 10^{-5} \text{ cm}^2/\text{s}$ [170], while the diffusion coefficient for K^+ is $D_{K^+} = 1.95 \times 10^{-5} \text{ cm}^2/\text{s}$ [170]. The liquid junction potential occurring between an electrode filled with KOH, and the surrounding solution with a different KOH concentration can have an impact on the measured potentials, which has to be considered when interpreting experimental data [171]. Details on the effect of the liquid junction potential for the experimental setup used in this work are discussed in paragraph 3.4.1.

2.4.4 Oxygen Effects during electrochemical H loading in Metals

Oxygen contamination can strongly affect the measured surface potential during loading, as will be presented in section 3.4.2, and must therefore be avoided for reliable results.

The effects of oxygen on the electrochemistry of metal electrodes for H storage has been investigated by Niessen and Notten [172], with the same electrolyte employed in this work. In their work, they charged $Mg_{74.5}Sc_{25.5}$ thin films in 6M KOH and observed how the oxygen content of the electrolyte affected the resulting potential response and electrochemical isotherms. The oxygen content in the electrolyte was minimized by bubbling it with high-purity Ar gas.

In their work, Niessen and Notten observe that the presence of oxygen in the electrolyte affects both the measured equilibrium potential and the estimated hydrogen content in the metal electrode. Moreover, they notice that during stepwise hydrogen loading the potential curves are less stable when the electrolyte contains oxygen, while they tend to approach a stable equilibrium potential with the purged electrolyte.

When oxygen is present in the electrolyte, the metal surface potential is not only controlled by the H loading reaction introduced in Eq. 2.23. In fact, a second reaction involving O_2 can happen at the sample's surface, namely [172]:



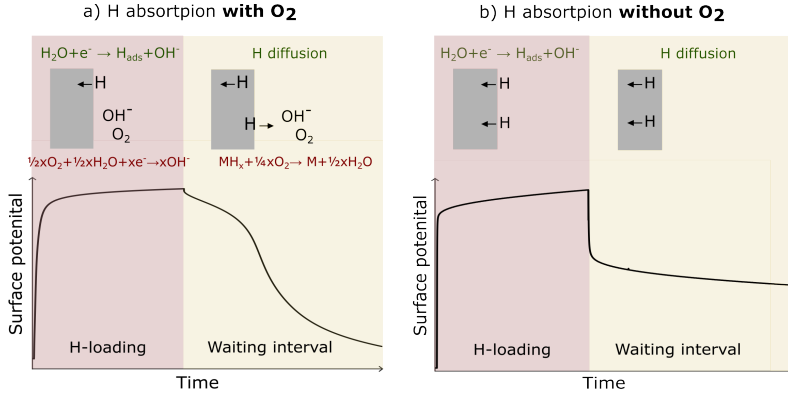
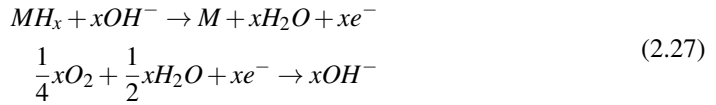


Figure 2.22: Reactions happening at the sample's surface during hydrogen absorption in KOH with O_2 (panel a) and without O_2 (panel b). In the loading interval a current is applied, leading to hydrogen adsorption on the metal electrode. Afterwards, when the current is no longer applied in the waiting interval, part of the hydride decomposes in the presence of O_2 , leading to a steep decrease of the surface potential (panel a). Without O_2 no hydrogen is lost in the waiting interval, leading to a more stable surface potential (panel b).

where the metal hydride MH_x is decomposed and oxygen is reduced at the metal-electrolyte interface according to the reaction chain [172]:



Therefore, even when no external current is applied, O_2 can be reduced at the metal's surface. The electron necessary for the reduction is obtained by decomposing part of the metal hydride MH_x . This second reaction has a higher equilibrium potential compared to the H loading one [172]. Therefore, when both reactions are happening at the sample's surface, the overall potential value will be shifted towards zero compared to the true equilibrium potential associated to the given H concentration. This explains the shift in the isotherms plateau value when oxygen is not purged from the electrolyte. Moreover, the shifted potential will drive the decomposition of the hydride phase according to Eq. 2.27, until the hydrogen content in the metal sample is completely depleted, explaining the instability of the potential curves during hydrogen loading in the presence of O_2 . On the contrary, when the oxygen content is negligible, the hydride phase cannot be decomposed unless a current is applied (Eq. 2.23) and a stable equilibrium potential can be reached after H loading. The parasitic reaction in Eq. 2.26 also explains the overestimation of the total hydrogen content, as part of the applied current does not contribute to hydrogen formation but is instead used for O_2 reduction. The competing reactions happening during hydrogen loading in the presence of oxygen and their effect on the surface potential are further visualized in Figure 2.22.

To summarize, oxygen content in KOH strongly influences the electrochemistry of H loading in metal samples. This leads to unstable potentials, overestimation of the hydrogen content and a shift in the measured equilibrium potential. Therefore, the oxygen content in the electrolyte must be controlled to obtain reliable data. The measures adopted in this work to minimise the oxygen content of the electrolyte are discussed in paragraph 3.4.2.

3 Materials and Methods

This chapter introduces the experimental methods developed and used during this work to study the effects of HPT on Mg and ZK60 discs, and to characterize hydrogen absorption in samples with different microstructures. Firstly, the sample's microstructure was refined by HPT, and the samples were prepared for hydrogen absorption as described in section 3.1. To understand the role of grain boundaries and other defects on hydrogen absorption, the samples' microstructure was characterized by electron microscopy, as introduced in section 3.2, and by x-ray diffraction, as introduced in section 3.3. Moreover, the sample's dislocation density and chemical composition was studied by positron annihilation spectroscopy, as described in section 3.7.

Hydrogen absorption was then studied by electrochemical and gas-phase loading for samples with different chemical compositions and deformation states. Regarding room temperature electrochemical loading, the necessary improvements to the experimental setup, together with considerations on the correct conversion between measured chemical potentials and equivalent hydrogen pressures are discussed in section 3.4. Moreover, section 3.4 reports preliminary results on palladium samples, which validate the loading experimental setup. Section 3.5 deals with hydrogen gas absorption at room temperature and at 398.2 K. A formula was developed to relate the amount of absorbed hydrogen to the measured pressure drop at 398.2 K, which is also introduced in section 3.5. Finite elements simulations were performed for a clearer interpretation of absorption results, and to better understand heat transport in the gas loading setup at 398.2 K. The developed models for FEM simulations are introduced in section 3.6.

3.1 Sample Preparation

3.1.1 Cutting and grinding of Mg discs

Mg and ZK60 samples were purchased in the form of extruded rods. Mg rods with a 10 mm diameter and 99.98% purity were purchased from HMW Hauner GmbH, while ZK60 (Mg- 6 wt.% Zn – 0.6wt.% Zr) rods with a 12 mm diameter were supplied by Helmholtz-Zentrum Hereon GmbH. The ZK60 rod was extruded at a temperature of 573 K with a speed of 3.3 mm/s. From these rods, discs of 0.8 mm thickness and 10 mm diameter were cut using an engine lathe at the

IAM-WK mechanical workshop. The discs' surface was then manually ground with SiC papers of grit 1000, 2500, and 4000 using isopropanol as a medium. Isopropanol was chosen to prevent oxidation of the surface during grinding.

3.1.2 Sputter coating with palladium

To allow hydrogen absorption in the cut and grinded samples at room temperature, the discs were coated with a palladium layer after removing the Mg oxide layer in vacuum. Coating with Pd has two positive effects: on the one hand, it prevents further oxide formation on the magnesium surface after exposing the sample to air, and on the other hand, it facilitates hydrogen absorption during gas-phase loading by allowing the splitting of hydrogen molecules, as explained in section 2.3.1.

The surface oxide removal and Pd coating was performed with the UHV Ar-ion beam sputter system of the DiM group at IAM-WK. For details regarding this system see Ref. [173]. The background pressure in the sputter chamber was always below 1×10^{-8} mbar. During sputtering, the argon pressure was 1.4×10^{-4} mbar, with a 99.9999% purity of the gas. The surface oxide was eliminated via sputter erosion, by exposing the magnesium surface directly to the Ar-ion beam for 30 minutes. Afterwards, the sample was rotated by 90° without breaking the vacuum condition and Pd was deposited on the clean surface for 4 hours. A special sample holder which allows rotations by 90° was used to maintain the UHV condition between the surface cleaning and the Pd deposition preparation steps. The thickness of the deposited layer, which can be calculated from the Pd sputter rate of 2 nm/min, is 480 nm. The sputter rate was evaluated by sputtering a Pd thin film on a Al_2O_3 substrate for 10 minutes in the same conditions, and then measuring its thickness by XRR.

Since during the oxide removal and Pd deposition steps the sample's temperature increases, the coating was performed before High-Pressure Torsion deformation to avoid modifying the refined microstructure.

3.1.3 High-Pressure Torsion deformation

High-Pressure Torsion (HPT) was employed to refine the microstructure of the disc samples prepared according to the previous sections. HPT was performed in collaboration with Dr. Julia Ivanisenko at INT, in a setup allowing for quasi-constrained deformation (see section 2.2.1). The employed anvils had a depth of 0.3 mm and a diameter of 11 mm. A hydrostatic pressure of 5 GPa was applied during deformation, and a total of 3 or 5 turns were performed at a speed of 1 rpm. The hydrostatic pressure of 5 GPa is sufficient to avoid cracking during HPT of magnesium

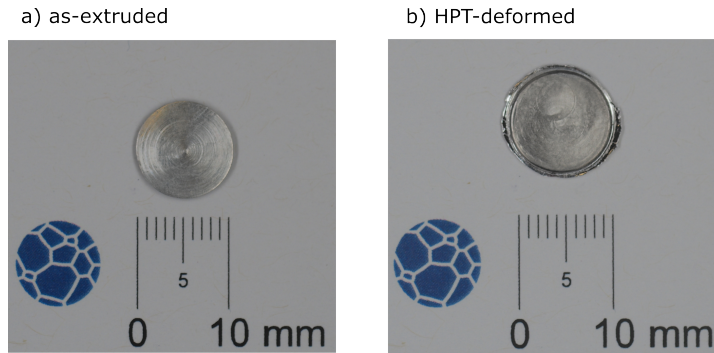


Figure 3.1: a) as-extruded ZK60 disc. b) ZK60 disc after HPT deformation. The disc's diameter increases after HPT.

alloys [42]. The introduced shear strain γ can be calculated according to equation 2.1. The shear strain is zero in the centre of the sample and increases linearly moving towards the edge. For the used sample geometry, a shear strain of respectively $\gamma = 173$ and $\gamma = 287$ was applied at the edge of the sample for $N = 3$ and $N = 5$ rotations.

Because of the anvils' shape, the discs resulting from HPT have a thickness of 0.6 mm and a diameter of 11 mm; they are therefore thinner than the initial Mg discs and have a larger surface area. The variation in the discs' appearance caused by HPT can be seen in Figure 3.1. The thickness of individual samples was measured before and after HPT using a micrometer screw. This sample geometry variation has to be taken into account when comparing the hydrogen content of samples in different deformation states.

3.2 Electron Microscopy

Electron microscopy is a powerful tool for investigating the morphology, microstructure, and composition of materials across length scales ranging from the micrometer down to the atomic level. In this work, both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed. In both techniques, a focused beam of high-energy electrons interacts with the specimen, generating a variety of signals that can be used to extract structural and chemical information.

In SEM, the electron beam is raster-scanned across the sample surface, and the resulting signals originate primarily from near-surface interactions. Different types of emitted electrons provide complementary information: secondary electrons, generated by inelastic scattering processes, are highly surface-sensitive and are commonly used to obtain high-resolution topographical contrast. Backscattered electrons, arising from elastic scattering events, are sensitive to the atomic number of the constituent elements and thus provide compositional contrast. Moreover, BSE and SE

provide channeling contrast, making different crystal orientations visible. In addition, energy-dispersive X-ray spectroscopy (EDS) was used in conjunction with SEM to analyze the elemental composition of the samples by detecting characteristic X-rays.

In TEM, a high-energy electron beam is transmitted through a thin specimen. The transmitted and diffracted electrons carry information about the crystallographic structure of the material. Spectroscopic methods such as electron energy loss spectroscopy (EELS) provide insight into the electronic structure and local chemical environment by analyzing the energy distribution of primary electrons after interaction with the sample. Scanning transmission electron microscopy (STEM), particularly in high-angle annular dark-field (HAADF) mode, was also employed to obtain Z-contrast images with high spatial resolution, enabling compositional and structural analysis.

Details about SEM and TEM experiments performed in this work are given in the following sections. Further information regarding these methods can be found in textbooks such as Goldstein et al. for SEM [174] and Carter et al. for TEM [175].

3.2.1 Scanning Electron Microscope (SEM) observations

The microstructure of Mg and ZK60 discs was characterized by Scanning Electron Microscopy (SEM) micrographs, correlated with Electron Diffraction spectroscopy (EDS) analysis, in collaboration with Dr. Sabine Schlabach and Gabriele Palazzo (IAM-WK, KNMFi). A Zeiss AURIGA SEM was used. The samples were prepared by cold embedding in Epoxy resin. Afterwards manual grinding was performed with SiC papers with grit 600, 1000, 2500 and 4000. The samples were then polished with 3 μm and 1 μm diamond suspensions. The final polishing step was performed with Etosil E; this polishing suspension is particularly suitable for magnesium as it is water-free and therefore prevents the formation of magnesium oxide or hydroxide on the polished surface. The used polishing parameters are reported in Table 3.1. ZK60 and Mg discs were

Table 3.1: Polishing parameters for the metallographic preparation of Mg and ZK60 samples.

Duration:	2.5 min
Pressure:	10 N (single)
Rotation direction:	opposite
Rotation speed:	60 (head)
	150 (base)

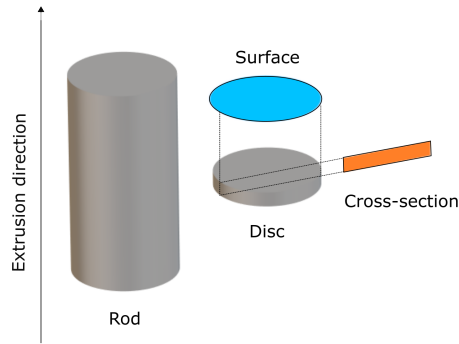


Figure 3.2: Characterized surface for Mg and ZK60 discs. The discs were cut from an extruded rod. The surface of the discs is perpendicular to the extrusion direction. Additionally, a cross-section parallel to the extrusion direction was observed.

observed on the surface perpendicular to the rod extrusion direction, and on the cross-section parallel to the extrusion direction as shown in Figure 3.2. On ZK60, some cross-section observations were also performed using a Ga FIB to create a surface parallel to the extrusion direction.

Overall, the metallographic preparation of magnesium samples is a delicate process because of the softness on the material, which easily leads to scratching, and because of its susceptibility to oxidation in water. To avoid oxidation problems, the polishing steps with diamond suspensions were performed using an alcohol-based lubricant, and water-free Etosil E was used for the final polishing step. While the grinding steps were performed using water as a lubricant, the samples were quickly dried with compressed air after grinding and then cleaned in a ethanol ultrasonic bath for 5 minutes between each preparation step.

To prevent scratching, the duration of the grinding steps should be as short as possible, while at the same time completely eliminating the deeper scratches from the previous step. For this reason, the samples were grinded manually, while often observing the resulting surface under an optical microscope and stopping as soon as the scratches from the previous step disappeared. A smaller sample area also helps achieving a scratch-free sample, because of the shorter time necessary to obtain a homogeneous surface during grinding. For polishing, a relatively low pressure is sufficient to achieve good results.

For ZK60 samples, it should also be noticed that intermetallic precipitates of size $\sim 1\ \mu\text{m}$ are present on the surface (see section 4.1), which may detach during polishing and also cause scratches, in particular while polishing with the $1\ \mu\text{m}$ diamond suspension. To minimize this issue, separate polishing cloths should be used for magnesium and for ZK60, and the ZK60 polishing cloths should be exchanged frequently.

3.2.1.1 Grain Size Analysis

The grain size distribution of Mg and ZK60 sample in different deformation states was analyzed from SEM images using the line intersection method, with the Matlab program Linecut [176]. The grain length was measured across 10 parallel lines, each crossing about 10-20 grains, and plotted in a histogram. The resulting distribution was then fitted with a lognormal function, returning the mean value and the variance of the grain length. The mean length estimates the average grain size, while the variance gives an estimate of the broadness of the resulting distribution. To exclude orientation effects the analysis was repeated using vertical lines. The line orientation did not affect the obtained distributions.

3.2.2 Transmission Electron Microscope (TEM) in-situ hydrogen loading

ZK60 samples were studied by in-situ hydrogen loading in different deformation states. Hydrogen uptake and release in ZK60 samples was studied by in situ TEM with the in situ gas cell Atmosphere AX from Protochips in a ThermoFisher Scientific Themis Z electron microscope in collaboration with Dr. Svetlana Korneychuk (IAM-WK and INT). For that, the samples were prepared and coated with palladium as described in section 3.1. Lamellas were then created for TEM investigations using the FIB-SEM TFS Helios 5 CX system (KNMFi). No strong interaction of the Ga-ion beam with the sample was observed. Different combinations of hydrogen pressure and temperature were studied, ranging from 298 K to 423 K.

Before in-situ loading the samples were characterized by STEM HAADF imaging and EDS mapping. The α -Mg to MgH_2 phase transformation was observed by Electrons Energy Loss Spectroscopy (EELS). Here, the transition from magnesium to magnesium hydride is visible through the shift of the bulk plasmon peak from 10.4 eV for Mg to 14.6 eV for MgH_2 [115, 177]. EELS maps were created to visualize the spatial distribution of the hydride phase with a resolution of 20 nm. After hydrogenation, the sample was dehydrogenated by removing the hydrogen atmosphere while maintaining a constant temperature, which drives the decomposition of the hydride phase. The dehydrogenated state was also observed by STEM HAADF imaging. During hydrogenation, the electron beams was blanked since high currents may lead to dehydrogenation. Therefore, the sample was only dehydrided when decreasing the hydrogen pressure in the atmosphere holder.

3.3 X-ray Diffraction

X-ray diffraction (XRD) is a widely used technique for the characterization of crystalline materials. It is based on the elastic scattering of x-rays by the periodically arranged atoms in a crystal lattice. When the Bragg condition is fulfilled, constructive interference gives rise to diffracted peaks at specific angles, which are related to the crystal structure and interplanar spacings. Since its development in the early twentieth century following the formulation of Bragg's law [178], XRD has become a standard method in materials science, solid-state physics and chemistry. It is commonly used for phase identification, structural analysis and texture characterization. A complete treatment of XRD can be found in textbooks such as Girolami et al. [179].

In this work, XRD measurements were used to investigate the diffraction spectra of magnesium and ZK60 discs in different deformation states. Diffraction spectra were employed to identify the intermetallic phases present in ZK60 and to follow eventual changes caused by HPT. The ZK60 spectra were also compared to those of pure Mg.

The diffraction spectra were measured with a Rigaku SmartLab diffractometer at ITEP (KIT). The diffractometer is equipped with a Cu $K\alpha$ radiation source and a HyPix-3000 high-resolution 2D detector. The Rx/Ry attachment stage was used for sample alignment. The measurements were performed with Bragg-Brentano geometry, and a 2.5° soller slit. The diffraction spectra were measured varying the 2θ angle between 30° and 75° , with a step of 0.02° and a scan speed of $0.5^\circ/\text{min}$.

3.4 Electrochemical loading in 6M KOH

Hydrogen was introduced in the Pd-coated Mg discs by electrochemical reactions in 6M KOH and by gas-phase loading, as will be described in section 3.5. Electrochemical loading allows for a precise control of the introduced hydrogen concentration, as described in section 2.4.2. Moreover, to perform gas-phase loading the equilibrium potential for the Mg to MgH_2 phase transformation has to be known, in order to apply an appropriate overpotential. Since literature values for bulk magnesium at room temperature are scarcely available, electrochemical loading was used to measure the equilibrium potential for hydride formation, which can be transformed to an equivalent hydrogen pressure as will be discussed in section 3.4.1.

6M KOH was chosen as an electrolyte because of its alkaline pH of 14.778. In fact, magnesium is resistant to corrosion in water-containing solutions with a pH larger than ~ 10.5 , because of the formation of a protective magnesium hydroxide layer on the surface [27]. On the contrary, magnesium is strongly corroded in more acidic solutions [27]. Although the samples are coated

with palladium, it is possible that small areas on the magnesium surface may be exposed to the electrolyte due to an imperfect coating, especially after HPT deformation. Therefore, it is necessary to use an electrolyte that would not lead to Mg corrosion. Moreover, the high concentration of OH^- ions guarantees stable surface potentials which are only affected by the hydrogen concentration in the sample, as explained in section 2.4.1.3. Finally, this electrolyte is used in literature for electrochemical loading of Mg samples, allowing for a direct comparison of the experimental results [168, 180].

To control the loading conditions and to adjust the proper loading potentials, the involved reactions were initially studied by Cyclic Voltammetry in Mg thin films [92] and are identified with: $Pd + xH_2O + xe^- \rightarrow PdH_x + xOH^-$ during hydrogen loading and $PdH_x + xOH^- \rightarrow xH_2O + Pd$ during hydrogen unloading [168, 172, 180]. The reactions are referred to palladium since the sample is in contact with the electrolyte only through the Pd-coated surface. Therefore, to achieve hydrogen loading a cathodic current has to be applied between the sample's surface and a counter electrode, while an anodic current leads to hydrogen desorption. After absorption in Pd, H diffuses into the Mg due to the larger site energy, according to Sieverts' law. In fact, following Sieverts' law (eq. 2.5), the higher concentration of hydrogen in palladium compared to magnesium would create a chemical potential gradient, leading to the diffusion of hydrogen towards magnesium. Since the Mg to MgH_2 phase transformation happens at a lower chemical potential compared to the Pd to $PdH_{0.6}$ phase transformation, the potential related to magnesium hydride formation will be observed first during loading, in equilibrium with a solid solution of hydrogen in palladium.

The used experimental setup consisted in a three-electrode cell connected to a potentiostat in galvanostatic mode (LPG03 from Bank Electronic). The used electrochemical cell is represented in Figure 3.3. This cell was designed in collaboration with Fabian Fink (IAM-WK) to allow for continuous hydrogen bubbling during loading, and manufactured at the IAM-WK mechanical workshop. The importance of bubbling is further highlighted in section 3.4.2. The sample was the working electrode (WE), a Hg/HgO electrode filled with 1M KOH (model HgO10 from Sensortechnik Meinsberg) was used as reference electrode (RE), while a palladium hydride sheet with a 1 cm^2 area was used as the counter electrode (CE). The sample was in contact with the electrolyte only through the Pd-coated surface exposing an area of 0.5 cm^2 (see Figure 3.3).

The sample was loaded stepwise by applying current pulses with a duration of 90 s and two different current intensities of $j = 80\mu A/\text{cm}^2$ and $j = 20\mu A/\text{cm}^2$. After the loading pulse, a waiting interval of 30 min was observed to allow hydrogen diffusion from the Pd coating towards magnesium as previously described. This interval was chosen empirically, to obtain sufficiently stable values of the measured potential over time, as shown in section 4.3.1.

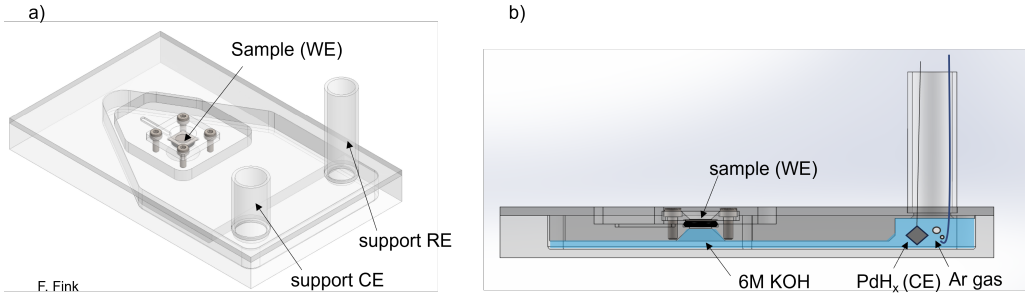


Figure 3.3: Cell used for electrochemical loading of Mg samples. a) 3-dimensional view with the sample and the supports for the counter electrode (CE) and the reference electrode (RE). b) lateral view of the electrochemical loading cell. The sample (WE) was placed horizontally in contact with the electrolyte. The Pd hydride counter electrode was placed next to a tube delivering high-purity Ar gas. The reference electrode (not shown) was placed behind the counter electrode with a similar support tube. This cell design allows for continuous bubbling of the electrolyte during loading experiments.

The WE potential, also known as electromotive force (EMF), was recorded during the whole loading process using the Bank Electronic LPG03 potentiostat, and the final value after 30 minutes was used to build EMF-concentration isotherms, where the achieved equilibrium potential is plotted as a function of the hydrogen content in the sample (see section 2.4.2). The amount of absorbed hydrogen n_H in moles can be directly calculated from the duration and intensity of the current pulse according to Faraday's law (Equation 2.25). By applying Faraday's law, we assume that all the hydrogen produced on the WE surface is then absorbed in the metal. This is not strictly true, as part of the absorbed hydrogen atoms can recombine in H_2 gas molecules and desorb from the sample's surface. Desorption is particularly relevant when high current densities are applied [92], while when the current density is sufficiently low, the error introduced by H_2 desorption becomes negligible. The loading conditions were optimized by tuning the applied current densities in order to minimize hydrogen desorption. This was tested with known systems, such as a Pd bulk and thin films, as reported in section 3.4.3.

In EMF-concentration isotherms the hydrogen content is often given as the number of hydrogen atoms per metal atom c_H , which is obtained by dividing n_H (Eq. 2.25) by the number of magnesium atoms in the sample $n_{Mg} = V_{sample}/V_{Mg}^{mol}$. This quantity would be misleading when comparing bulk and HPT-deformed samples loaded with the same parameters, because the disc thickness decreases from 0.8 to 0.6 mm after High-Pressure Torsion while the surface area exposed to the electrolyte remains constant, leading to a smaller sample volume which would artificially increase the calculated H concentration in HPT samples. The same hydrogen concentration in samples of different volumes could be achieved by varying the applied current intensity and duration according to Eq. 2.25. However, the applied current step also has an effect on the measured

isotherms, as will be presented in section 4.3.2; it is therefore not advisable to directly compare isotherms obtained with different loading parameters. To avoid these issues, the hydrogen content in Mg samples is given as an equivalent hydride thickness t_{MgH_2} :

$$t_{MgH_2} = \frac{n_H}{2} \cdot \frac{V_{mol}^{MgH_2}}{A} \quad (3.1)$$

where $A = 0.5\text{cm}^2$ is the area exposed to electrolyte and $V_{mol}^{MgH_2}$ is the molar volume of MgH_2 . This approach is justified by the fact that a hydride blocking layer forms rapidly in magnesium samples, as described in section 2.3.5.

3.4.1 Conversion of the equilibrium potential to an equivalent hydrogen pressure

To compare the results of electrochemical and gas-phase loading, the measured equilibrium potential can be converted to an equivalent hydrogen pressure according to Nernst's equation. The conversion is based on relating the surface potential measured against the Hg/HgO reference electrode to the Hydrogen Electrode potential.

Electrode potentials are often given in reference to the Standard Hydrogen Electrode (SHE), which is commonly used as a reference in electrochemistry. The hydrogen electrode consists in a Pt black electrode inserted in an electrolyte and bubbled with H_2 gas. The reaction occurring at the electrode surface is: $H^+(aq) + e^-(m) \leftrightarrow \frac{1}{2}H_2(g)$, where the dissociation and recombination of H molecules are mediated by adsorption on the electrode's surface [166]. The equilibrium condition for the Hydrogen electrode can be expressed through Nernst equation as [166]:

$$E = E_0 - \frac{RT}{2F} \ln \left(\frac{p_{H_2}}{a_{H^+}} \right) \quad (3.2)$$

where p_{H_2} is the H gas pressure and a_{H^+} is the activity of the H^+ ions. The Standard Hydrogen Electrode is a hydrogen electrode where the H gas pressure is 1 atm and the activity of the H^+ ions is 1, which corresponds roughly to a 1M concentration.

The Hg/HgO reference electrode is based on solid HgO and liquid Hg, in an aqueous solution of KOH or NaOH [171]. The reaction determining the equilibrium potential is: $HgO(s) + H_2O(l) + 2e^- \leftrightarrow Hg(l) + 2OH^-$, the equilibrium condition according to Nernst equation is then [171]:

$$E = E_0 - \frac{RT}{2F} \ln \left(\frac{a_{OH^-}^2}{a_{H_2O}} \right) \quad (3.3)$$

where we assume the activity of solid HgO and liquid Hg to be 1. The potential of the Hg/HgO electrode against the hydrogen electrode can be calculated by knowing the formal potential of the Hg/HgO electrode $E_f(\text{Hg}/\text{HgO})$:

$$E_f(\text{Hg}/\text{HgO}) = E_0(\text{Hg}/\text{HgO}) - \frac{RT}{2F} \ln \left(\frac{a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \right) \quad (3.4)$$

where $E_0(\text{Hg}/\text{HgO}) = 0.98 \text{ V}$ [171] is the standard potential of the electrode and the second term takes into account the activity of the OH^- ions, which is determined by their concentration in the electrode solution. For an electrode filled with 1M KOH, we have $E_f(\text{Hg}/\text{HgO}) = 0.105 \text{ V}$ [171]. To complete the conversion we also need to consider the activity of the H^+ ions and the liquid-junction potential caused by the different KOH concentrations in the electrode (1M KOH) and in the surrounding electrolyte (6M KOH). The effect of the H^+ ions is accounted by adding the term $2.303 \cdot m \cdot RT/F$ to the effective potential, where m is the number of H^+ involved in the reaction (1 in the case of electrochemical hydrogen loading according to Eq. 2.23) [166, 171]. Considering $T = 298.15 \text{ K}$ and $m = 1$ this term becomes $0.0592 \times \text{pH}$. The liquid junction potential between 1M KOH and 6M KOH was calculated according to the stationary Nernst–Planck equation [181] using LJPcalc (RRID:SCR_025044), resulting in $E_{\text{LJP}} = 20 \text{ mV}$. Considering all the terms, and writing explicitly the hydrogen electrode potential we obtain:

$$\begin{aligned} -\frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}}{p_0} \right) &= E(\text{Hg}/\text{HgO}) + 0.0592 \times \text{pH} + E_f(\text{Hg}/\text{HgO}) + E_{\text{LJP}} \\ &= E(\text{Hg}/\text{HgO}) + 0.9599 \text{ V} \end{aligned} \quad (3.5)$$

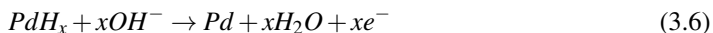
where $p_0 = 1 \text{ atm}$, $E(\text{Hg}/\text{HgO})$ is the potential measured against the Hg/HgO electrode and $\text{pH} = 14.778$ was considered for 6M KOH. The pH value was calculated for 6M KOH with the tool developed by Hausmann et al. [182]. Equation 3.5 was applied to convert the equilibrium potentials resulting from electrochemical loading to equivalent hydrogen pressures, allowing the comparison to gas loading results and literature values. It should be noted that the LJP contribution is smaller than the pH contribution (874 mV) and the formal potential of the RE (105 mV), but it cannot be neglected as it would still introduce a 2.5% error on the typical equilibrium potential of magnesium hydride formation ($\sim -800 \text{ mV}$ vs Hg/HgO).

3.4.2 Reduction of O_2 content in 6M KOH

As introduced in paragraph 2.4.4, the presence of oxygen in 6M KOH strongly influences the electrochemistry of the system and can have a strong influence on the measured potentials and H concentrations, as well as on the stability of the hydride phase. To minimize oxygen effects, its concentration in the electrolyte has to be reduced. In this work this was achieved in two ways:

firstly, by bubbling with 99.9999% Ar gas, and secondly, by employing a Pd hydride counter electrode (as described previously in section 3.4).

The Ar bubbling was performed for 30 minutes before starting the experiment and then continuously during the loading experiment; the effects related to electrolyte bubbling are reported in paragraph 3.4.2. The Pd hydride electrode was prepared by separately loading a Pd sheet of area 1 cm^2 and thickness 0.25 mm. The Pd sheet was loaded in 6M KOH using a current density of 0.25 mA/cm^2 and a Pt counter electrode of area 1 cm^2 . The loading was performed until a concentration of $\sim 0.08 \text{ H/Pd}$ was reached. This value was chosen to be in the two-phase region of the H-Pd phase diagram, where the hydride phase is stable, and to provide an adequate reservoir of hydrogen for the duration of the whole loading experiment. To achieve this, the amount of hydrogen in the counter electrode must be higher than what will be loaded in the working electrode. The electrochemical reaction happening at the Pd hydride counter electrode during H loading in magnesium is in fact the decomposition of Pd hydride according to [172]:



Therefore, if the palladium hydride electrode is sufficiently charged, this reaction provides an adequate current at the counter electrode without introducing oxygen in the electrolyte.

The combination of these two methods allows for a correct estimation of the hydrogen content and of the equilibrium potential during electrochemical hydrogen loading.

The effect of oxygen in the electrolyte on the measured surface potential of bulk Pd sheets is visualized in Figure 3.4. The sheets had a thickness of 0.25 mm and were loaded from one side with a surface area of 0.5 cm^2 , using a Pd hydride counter electrode. The H loading was performed by applying a current density of $j = 100 \mu\text{A/cm}^2$ for 90 s, and afterwards waiting 120 s for equilibrium. The loading step produces a concentration change of $3.3 \times 10^{-5} \text{ H/Pd}$ according to Eq. 2.25. The EMF curves are compared for no Ar bubbling, bubbling with Ar gas of unknown purity and bubbling with 99.9999% (6N) Ar gas.

When no bubbling is performed, the potential after 120 s is $\sim -100 \text{ mV}$ and appears to decrease from step to step with H concentration. Moreover, the potential curves do not reach stable values. When converting the potential of -100 mV to an equivalent H_2 pressure according to Eq. 3.5, we obtain an extremely low value of $p_{\text{H}_2} = 1.3 \times 10^{-26} \text{ mbar}$, which is incompatible with the achieved hydrogen concentration. The potential curves appear more stable when bubbling with 6N Ar gas, and show a potential around -800 mV , gradually increasing with H concentration. In this case the equivalent H pressure after the last step is $p_{\text{H}_2} = 4.3 \mu\text{bar}$. When bubbling with low-purity Ar gas, the potential curves only briefly show a potential value of $\sim -740 \text{ mV}$, before decreasing to $\sim -300 \text{ mV}$. The argon purity is unknown for this measurement because a leak in

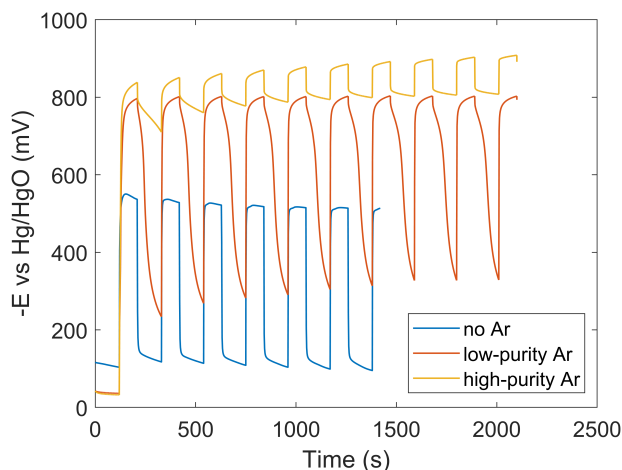


Figure 3.4: Time evolution of the surface potential during stepwise hydrogen loading of bulk Pd sheets. The Pd samples were loaded for 90 s at $100 \mu\text{A}/\text{cm}^2$, followed by a 120 s waiting period. The 6M KOH electrolyte was either not bubbled, bubbled with Ar gas of unknown purity or bubbled with 99.9999% Ar. Each loading step introduces a concentration of $\Delta c_H = 3.3 \times 10^{-5}$ H/Pd. While the recorded curves are stable for the high-purity Ar bubbling, a strong shift and instability of the potential curves is observed for low-purity Ar and for the measurement without bubbling.

the pipe connecting the argon bottle to the loading cell lead to mixing of an unknown amount of air with the high-purity Ar.

Overall, these results show how the electrolyte quality can have a dramatic effect on the measured surface potentials during electrochemical loading. When oxygen is present in the electrolyte, the recorded potentials are shifted towards zero, and the magnitude of the shift is influenced by the oxygen concentration (see also section 2.4.4). Moreover, the oxygen content prevents the surface potential from reaching a stable equilibrium value, due to hydrogen losses driven by the recombination of O_2 molecules and adsorbed hydrogen forming H_2O according to Eq. 2.27. The effectiveness of Ar bubbling and of the Pd hydride counter electrode in minimizing oxygen effects are further proved by the measured Pd isotherms in the following section.

3.4.3 Palladium electrochemical isotherms

The previous section shows how the combination of a Pd hydride counter electrode and bubbling with 99.9999% Ar gas limits hydrogen losses during electrochemical loading, leading to more stable potential curves. To verify that these measures allow to correctly estimate the achieved hydrogen concentration and equilibrium potential, the room temperature isotherms of bulk and thin film palladium were studied. Since the properties of this system are well known in literature, Pd isotherms can be used to validate the chosen loading conditions.

Table 3.2: Loading current density and intervals used for the isotherm in Figure 3.5.

Step	j (mA/cm ²)	Δt (s)	Δc_H (H/Pd)
1-16	1.4	1	5.2×10^{-5}
17-21	1.4	5	2.6×10^{-4}
22-23	1.4	10	5.2×10^{-4}
24-26	7.1	10	2.6×10^{-3}
27-40	14	10	5.2×10^{-3}

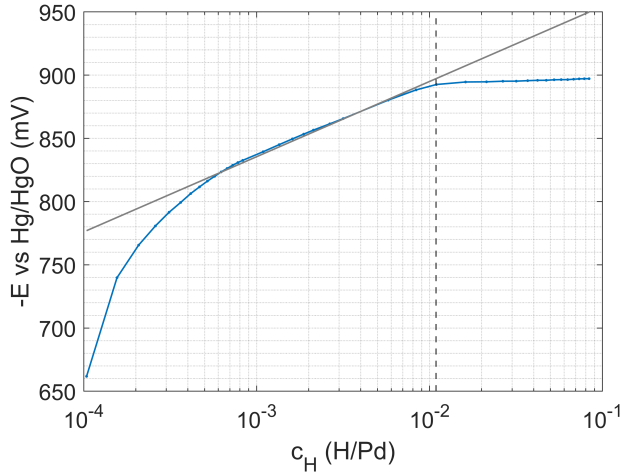


Figure 3.5: Electrochemical isotherm for a bulk Pd sheet of thickness $25 \mu\text{m}$, loaded according to Table 3.2. The solubility limit is $\sim 10^{-2}$ H/Pd, indicated by a dashed line in the figure. The equilibrium potential for Pd H formation is -910 mV. The relation between surface potential and hydrogen concentration in the solid solution phase according to Sieverts' law (Eq. 2.5) is represented as a gray solid line. The measured potential follows Sieverts' for $c_H > 5 \cdot 10^{-4}$ H/Pd, until it reaches the equilibrium value corresponding to palladium hydride formation.

First, results for bulk Pd are presented. Sheets with a thickness of $25 \mu\text{m}$ were investigated using the setup described in paragraph 3.4, from a concentration of $\sim 5 \times 10^{-5}$ H/Pd after the first loading step, to a final concentration of ~ 0.1 H/Pd. The applied concentration steps are reported in Table 3.2. A representative electrochemical isotherm is reported in Figure 3.5. We can observe the plateau region related to Pd hydride formation at a potential of -910 mV vs Hg/HgO. This value is compatible with potentials for Pd hydride formation measured in a similar electrolyte [168]. When converting the equilibrium potential to an equivalent hydrogen pressure according to Eq. 3.5, we obtain $p_{H_2} = 23$ mbar, which is compatible with the equilibrium values reported for Pd pressure-concentration isotherms at 293.15 K [183]. The transition from solid solution to hydride phase starts at a concentration of $\sim 10^{-2}$ H/Pd; this value also matches with literature values for bulk Pd such as in Ref. [97].

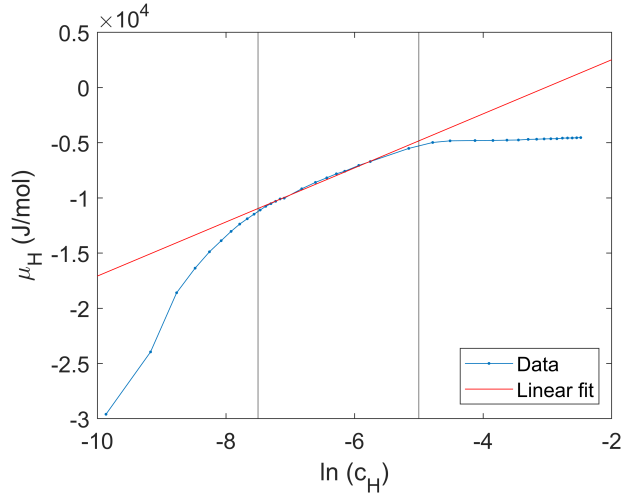


Figure 3.6: Chemical potential μ_H as a function of the logarithm of H concentration for a bulk sheet of Pd with $25\ \mu\text{m}$ thickness (calculated from the isotherm in Figure 3.5). The red line represents the results of a linear fit between -7.5 and -5, which corresponds to concentrations between $5.5 \cdot 10^{-4}$ H/Pd and $6.7 \cdot 10^{-3}$ H/Pd. The slope from the linear fit is (2.45 ± 0.13) kJ/mol, which matches with the slope expected according to Sieverts' law.

The dependence between the equilibrium potential and hydrogen concentration can further be investigated in the solid solution phase. The equilibrium potential (which is proportional to the hydrogen chemical potential), increases linearly with the hydrogen concentration for $c_H > 5 \times 10^{-4}$ H/Pd, while a deviation from this linear behavior is observed at lower concentrations. The linear portion of the isotherm is described by Sievert's law (see section 2.3.3), therefore we can expect $\mu_H \propto RT \ln(c_H)$; at 298 K the proportionality constant is $RT = 2.48$ kJ/mol. The chemical potential of hydrogen is calculated according to Eq. 3.5 and plotted against the logarithm of the hydrogen concentration in Figure 3.6. The portion indicated by vertical lines was used to perform a linear fit, resulting in a slope of (2.45 ± 0.13) kJ/mol, which is in agreement within the experimental error with the expected value of 2.48 kJ/mol. The deviation from Sievert's law at lower concentrations is caused by hydrogen trapping at defects whose energy is lower than that of interstitial sites [97].

Pd thin films of thickness 100 nm were also investigated. A representative electrochemical isotherm is reported in Figure 3.7. Here, the film is loaded with a current density of $j = 40\ \mu\text{A}/\text{cm}^2$ for 20 steps and then with $j = 60\ \mu\text{A}/\text{cm}^2$ for the remaining 8 steps. The loading step lasted 90 s, while the equilibrium potential is recorded after an interval of 120 s. As expected, the solubility limit is higher in thin films compared to bulk samples [97] – ~ 0.1 H/Pd for the thin film against ~ 0.01 H/Pd for bulk Pd – and the solid-solution portion of the isotherm has a steeper slope than according to Sieverts' law [97]. A steeper slope in the α -phase with respect to Sievert's law is expected for thin films because of the higher concentration of defects

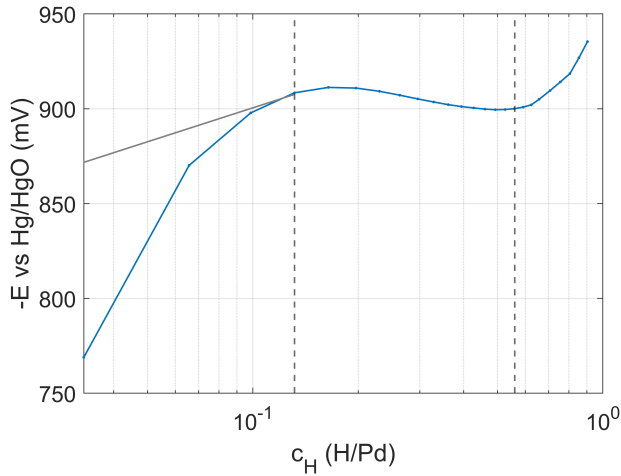


Figure 3.7: Room temperature isotherm for a 100 nm Pd thin film, loaded with $j = 40 \mu\text{A}/\text{cm}^2$ for 20 steps and then with $j = 60 \mu\text{A}/\text{cm}^2$ for 8 steps. The plateau for Pd hydride formation is at -900 mV , delimited by the two dashed lines at 0.13 and 0.56 H/Pd . The solid line represents the relation between potential and concentration according to Sieverts' law (Eq. 2.5). The solubility limit of hydrogen the α -phase is higher than for bulk palladium, and the potential in the α -phase is lower than what expected according to Sieverts' law, as previously observed for Pd thin films [97].

such as grain boundaries and dislocations lowering the chemical potential at low concentrations [97]. The higher defects concentration is also responsible for the increased solubility limit of hydrogen in metal thin films compared to bulk. The total hydrogen content in the hydride phase is 0.56 H/Pd , in agreement with the 0.6 H/Pd observed at room temperature for bulk and thin film samples [97, 183].

Overall, these results relating to H absorption in Pd confirm that the employed electrochemical loading setup can reliably measure the achieved equilibrium potential and hydrogen content, if the applied loading current densities are not too high. The highest current density used in this section was $j \sim 700 \mu\text{A}/\text{cm}^2$ (see Table 3.2) and did not lead to an overestimation of the absorbed hydrogen concentration according to Faraday's Law (Eq. 2.25).

3.5 Gas Volumetry

Gas volumetry was employed to study hydrogen absorption from the gas phase and hydride formation at room temperature and at 398.2 K . The used experimental setups are described in this section.

3.5.1 Hydrogen loading at room temperature

For room temperature hydrogen absorption, a Sievert's type apparatus was used, as shown in Figure 3.8.

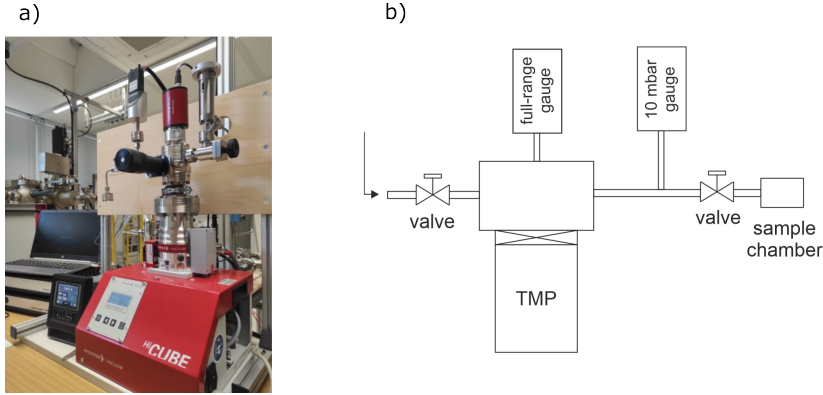


Figure 3.8: a) Setup built for room temperature gas volumetry experiments. b) Scheme of the main components of the setup. The hydrogen pressure can be set using a 10 mbar range gauge before introducing the gas to the sample chamber.

The samples were exposed to a pressure of $P_0 = 0.1 \text{ mbar}$ H_2 gas (6N purity) in a chamber with a fixed volume of $V = (90 \pm 1) \text{ cm}^3$. The background pressure of the vacuum chamber was measured with a Pfeiffer PKR 360 full-range gauge and was below $3 \times 10^{-8} \text{ mbar}$. As hydrogen is absorbed in the sample from a closed chamber with a fixed volume, the hydrogen pressure in the chamber drops. The pressure drop was recorded with a MKS 10 mbar Baratron Range pressure gauge with a sensitivity of 10^{-4} mbar , while the temperature in the chamber was recorded using a thermocouple. The loading pressure was chosen to be above the equilibrium pressure for hydride formation at room temperature, which is expected to be in the $1 \mu\text{bar}$ range according to Eq. 2.7. A more precise measurement of the equilibrium pressure for hydride formation in Mg and ZK60 at room temperature was obtained by electrochemical loading and was $\sim 4 \mu\text{bar}$ for Mg and $\sim 10 \mu\text{bar}$ for ZK60 (see section 4.3.2). Therefore, the chosen pressure of $100 \mu\text{bar}$ provides an adequate driving force to hydride nucleation.

The amount of absorbed hydrogen in moles can be calculated from the pressure drop in the vacuum chamber $P_0 - P_f$ at a temperature T through ideal gas equation:

$$n_H = 2 \cdot \frac{(P_0 - P_f)V}{RT} \quad (3.7)$$

the factor 2 accounts for the splitting of the H_2 molecule to atomic H upon absorption. The behavior of hydrogen at the chosen pressure and temperature can be approximated to that of an ideal gas [184]. The uncertainty on n_H was estimated through a gaussian error propagation, by quadrature summation of the uncertainty on the measured pressure drop ΔP , on the chamber volume ΔV and on the temperature ΔT . While the uncertainty on the pressure drop is given by the instrument sensitivity, for the measured temperature small fluctuations during measurement prevail as the larger source of error and were therefore used to evaluate ΔT .

After hydrogen was absorbed to an equilibrium content during each loading step, leading to a respective constant pressure value P_f , the vacuum chamber was again filled to $P_0 = 0.1$ mbar and a new absorption curve was recorded. This process was repeated until no more hydrogen was absorbed by the sample, resulting in stepwise loading with a uniform driving force to hydride formation within the different loading steps. To exclude effects on the measured pressure which are not related to hydrogen absorption, calibration measurements were performed without introducing any sample in the sample chamber, showing a stable value of the recorded pressure over time and confirming that the measured pressure drops are indeed related to hydrogen absorption in the magnesium samples.

3.5.2 Hydrogen loading at 398.2 K

Together with room-temperature hydrogen absorption, gas loading was also performed at 398.2 K, to investigate if the microstructure effects observed at room temperature are still active at higher temperatures. This temperature was chosen as the midpoint between room temperature and the often studied loading at 573 K (see section 2.3.9).

Figure 3.9 shows the experimental setup used for gas loading at 398.2 K. The sample was placed inside a borosilicate tube, which was partly inserted in an oven. The temperature in the oven was controlled using an oven with a Eurotherm 902s PID controller. The temperature inside the

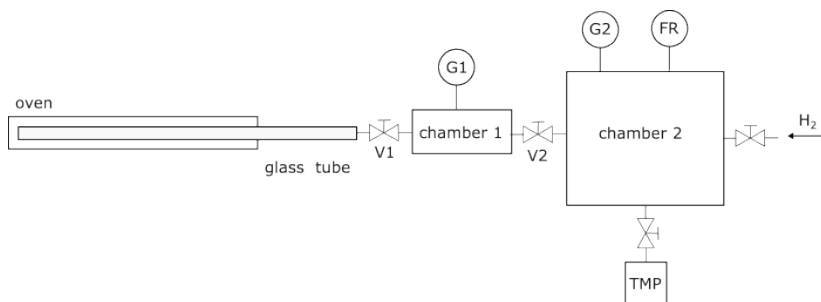


Figure 3.9: Schematic representation of the experimental setup used for gas loading at 398.2 K. Only part of the setup is introduced in the oven with a 398.2 K temperature, while the rest is at room temperature.

oven was measured with a thermocouple fixed to the outside surface of the glass tube and set to 398.2 K. After an initial adjustment phase, which happened before exposing the sample to hydrogen gas, the external temperature of the glass tube was (398.2 ± 0.1) K.

Before starting the heating and H absorption experiment, a background pressure below 6×10^{-8} mbar was achieved in the whole system, measured with a full-range Balzers PKR251 pressure gauge (indicated as FR in Figure 3.9). Chambers 1 and 2 were used to set the initial hydrogen pressure of 40 mbar in the system, maintaining the valve V1 closed. For the absorption measurement, valve V2 was closed and V1 was subsequently opened, leading to a pressure close to 20 mbar in the glass tube and chamber 1. The pressure evolution over time was then recorded using a mks Baratron AA01A pressure gauge (G1) in the glass tube and chamber 1, where a pressure drop is expected as a consequence of hydrogen absorption in the sample. The gauge range is 1- 1000 Torr. The pressure evolution was also monitored in chamber 2 using a mks Baratron AA01A pressure gauge (G2), where pressure variations can be attributed to the gauge drift and to temperature fluctuations. More details about gauge drift estimation and correction are reported in section 4.5.2. The temperature was also monitored on the external wall of chamber 1 using a thermocouple. After loading, the sample was unloaded by removing the hydrogen gas in the glass tube and in chamber 1, returning to a background pressure below 10^{-4} mbar, and keeping the oven temperature at (398.2 ± 0.1) K. Afterwards, V2 was closed again and the hydrogen release was monitored by measuring the pressure increase over time in the glass tube and in chamber 1. The loading-unloading cycle was repeated 5 times for undeformed and HPT-deformed ZK60 samples prepared according to section 3.1.

When evaluating the absorption curves in this gas-loading setup, the non-uniform temperature in chambers 1 and 2 must be taken into account. In fact, the total volume of the glass tube is (91 ± 1) cm³, with a length of 51.3 cm and an internal diameter of 1.5 cm. Of the total length, only 36 cm are inserted on the oven, reaching a temperature of 398.2 K, while the rest of the tube, as well as the rest of the vacuum system, is at room temperature. Chamber 1 has a volume of (90 ± 1) cm³. Therefore, during the loading experiment the pressure drop following hydrogen absorption in the sample is measured over a volume of ~ 180 cm³, of which around 1/3 is at 398.2 K, while the remaining 2/3 is at room temperature.

This setup complicates the relation between the measured pressure drop and the amount of hydrogen absorbed in the metal sample compared to the room temperature case in Equation 3.7, where a constant temperature can be assumed for the whole hydrogen volume. Hence, the relation of the moles of absorbed H₂ molecules n_{abs} and the respective pressure drop ΔP for the condition of two connected gas volumes V_1 and V_2 at different temperatures T_1 and T_2 was derived. More details on the derivation are given in the Appendix A. The main assumptions are that the gas behaves ideally, that the pressure is uniform in the whole system and that the system

is closed, so that the total number of hydrogen molecules is conserved. In these conditions we have:

$$\Delta P = R \frac{T_1/V_1 \cdot T_2/V_2}{T_1/V_1 + T_2/V_2} n_{abs} \quad (3.8)$$

This formula is used to calculate the moles of absorbed hydrogen from the measured pressure drop ΔP . The assumption of a uniform pressure might not be true for very small chambers, or for chamber connected through a pipe with a small cross section; it is however a reasonable assumption for this experimental setup.

Figure 3.10 shows the relation between a pressure drop ΔP and the absorbed hydrogen n_{abs} in different conditions for the experimental setup in Figure 3.9. Assuming that the whole sample chamber and chamber 1 are at 400 K would lead to an underestimation of n_{abs} , while assuming that the whole system at 300 K would lead to its overestimation. Using Equation 3.8 we can predict the relation between ΔP and n_{abs} , considering as V_1 the portion of the sample chamber inserted in the oven, and as V_2 the remaining part of the sample chamber together with chamber 1. This also leads to a linear relation between ΔP and n_{abs} , laying in between the two extremes where only one temperature was considered. In reality, this assumption is also a simplification, because the gas temperature does not drop immediately outside of the oven. To better understand the temperature evolution and the heat transport in the experimental setup during heating, FEM

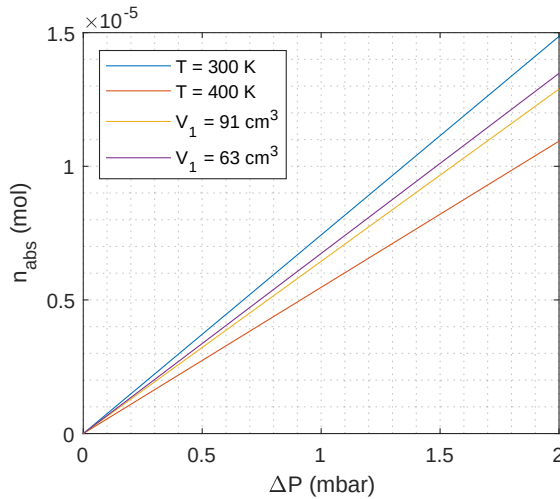


Figure 3.10: Absorbed moles of H_2 as a function of the measured pressure drop. For temperatures of 300 K and 400 K, the pressure drop is related to a volume of 181 cm^3 , corresponding to the sum of sample chamber (glass tube) and of chamber 1 in Figure 3.9. For the other lines, two volumes at different temperatures are considered. $V_1 = 63 \text{ cm}^3$ considers only the sample chamber portion inserted in the oven at 400 K and the rest at room temperature, while $V_1 = 91 \text{ cm}^3$ assumes that the whole sample chamber is at 400 K and that chamber 1 is at 300 K.

simulations were performed as described in section 3.6.2. In general it appears that, outside of the oven, the temperature drops gradually to room temperature over a transition zone that extends until the end of the glass tube. To account for this effect, a lower limit to the amount of absorbed hydrogen can be estimated by assuming that the whole glass tube is at 400 K and extending the heated volume to $V_1 = 91 \text{ cm}^3$. This line is also plotted in Figure 3.10, and lays close to the one for $V_1 = 63 \text{ cm}^3$. Since the unknown temperature profile is the main source of error in this experimental setup, the two lines in Figure 3.10 with the different values of V_1 have been used as the upper and lower limit when estimating the amount of absorbed hydrogen associated to the measured pressure drop.

3.5.3 Interpretation of absorption curves through the JMAK analysis

To gain quantitative insights into the nucleation and growth behavior of magnesium hydride from measured H_2 gas absorption curves, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) analysis can be used. This method can be generally applied to interpret the time dependence of a new phase formation [185–188], in this case the hydride phase. The volume fraction f of the new phase is represented as function of time t as:

$$f(t) = 1 - \exp(-Ct^n) \quad (3.9)$$

where C is a constant and n is the JMAK exponent. The value of n is related to the mechanism of phase transformation [189], in particular to the rate on nucleation, the growth dimension of the nuclei and whether the process is diffusion- or interface-limited. In fact, n can be calculated as: [189]:

$$n = \frac{d}{m} + N \quad (3.10)$$

where $d = 1, 2, 3$ is the growth dimension, $m = 1$ for interface-limited transformations and $m = 2$ for diffusion-limited transformations, and N indicates the nucleation rate, with $N = 0$ for a constant number of nuclei, $N = 1$ for a linearly increasing number of nuclei, etc. Values of the JMAK exponent n for different combinations of m , d and N are given in Table 3.3. By plotting $\log(-(1-f))$ as a function of $\log(t)$, the JMAK exponent can be obtained with a linear fit.

Considering a fast initial nucleation followed by the growth of a fixed number of nuclei, $n = 0.5$, $n = 1$ or $n = 1.5$ is expected respectively for 1D, 2D or 3D growth of the hydride nuclei in a diffusion-limited process. For an interface-limited process $n = 1$, $n = 2$ or $n = 3$ is expected respectively for 1D, 2D or 3D growth. If the number of new phase nuclei increases linearly with

Table 3.3: JMAK exponent n according to Eq. 3.10 for different growth dimensions d and nucleation rates N . The growth dimension goes from 1D to 3D. The nucleation rate is given for a constant density of nucleation sites ($N = 0$), for a linear ($N = 1$) and for a quadratic ($N = 2$) nucleation rate. The exponents are given both for diffusion-limited processes, where $m = 2$ is used in Eq. 3.10, and for interface-limited process, where $m = 1$ is used.

Process	$d \backslash N$	0	1	2
diffusion-limited ($m=2$)	1	0.5	1.5	2.5
	2	1	2	3
	3	1.5	2.5	3.5
interface-limited ($m=1$)	1	1	2	3
	2	2	3	4
	3	3	4	5

time, the JMAK exponent increases by a factor one; if the number of new phase nuclei increases faster than linearly, a higher exponent will be observed.

When interpreting the resulting JMAK exponent, it must be noted that different combinations of growth mode, nucleation mode and limiting process can lead to the same n value. For example, a

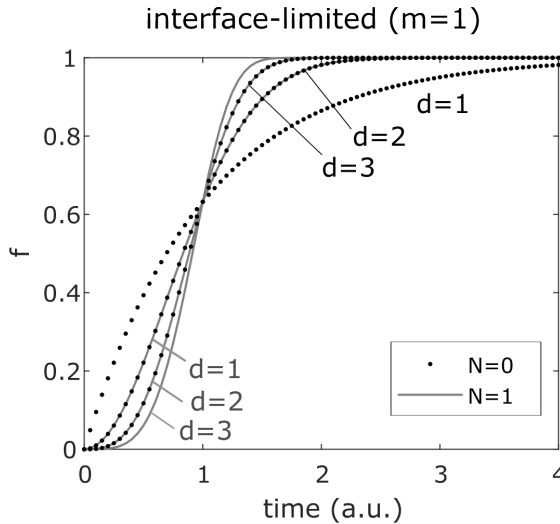


Figure 3.11: Transformed fraction f as a function of time for different combinations of growth dimension and nucleation rates according to Eq. 3.9. The curves are represented for an interface-limited transformation ($m = 1$ in Eq. 3.10). The dotted lines represent a constant number of nuclei ($N = 0$), while the solid lines are for a and linearly increasing number of nuclei ($N = 1$). In both cases, 1-dimensional to 3-dimensional growth is represented ($d = 1, 2, 3$). Some of the curves overlap, showing how different combinations of nucleation and growth modes can lead to the same observable.

JMAK exponent of $n = 1$ can be related to a diffusion-limited process with 2D growth of a fixed number of new phase precipitates, but also to an interface-limited process with 1D growth of a fixed number of precipitates or to a linearly increasing number of precipitates without growth. A further example for interface-limited growth is shown in Figure 3.11, where different combinations for d and N lead to the same time-dependence of the transformed fraction. Therefore, JMAK analysis alone is not sufficient to infer the mode of hydride formation, and it must be accompanied by other observations to resolve the ambiguity. In this work, hydride formation has also been directly observed by in-situ TEM.

3.6 Finite Element Simulations

The Finite Element Method (FEM) is used to discretize and numerically solve partial differential equations which cannot be solved analytically. The computational domain is divided into a finite number of small subdomains, referred to as elements, which are connected at points called nodes, forming a mesh. Within each element, the governing partial differential equations are discretized to numerical equations and solved. This leads to an approximation of the solution, whose accuracy depends on the choice of the mesh and of the boundary conditions. In particular, a finer mesh will lead to a more precise solution, at the expense of increased computation time and resources. Therefore, a common approach in this type of simulations is to simplify the studied geometry and to reduce the domain volume by taking advantage of symmetries, in order to achieve accurate results with reasonable computational efforts. Since its first formulation in the 1940s [190, 191], this method has been applied to different fields of physics and engineering, such as structural analysis, electromagnetism, heat transport and fluid dynamics.

In this work, FEM simulations were performed using the software Comsol Multiphysics 6.2. Two different aspects were addressed. Firstly, the role of grain boundary diffusion during electrochemical loading of MgH_2 samples with different microstructures was investigated, with particular focus on the time evolution of the Pd-coating surface potential. Secondly, FEM simulations were used to model the heat transport and temperature distribution during gas-phase hydrogen loading at about 400 K. Experimental details of the simulations are given in the following sections. A complete treatment of FEM, including the mathematical methods used to discretize and solve partial differential equations can be found in textbooks such as Bathe et al. [192].

3.6.1 Grain Boundary diffusion in MgH_2

To understand the role of grain boundary diffusion during electrochemical loading and their effect on the Pd surface potential, FEM simulations were conducted using the Transport in Solids module of Comsol Multiphysics 6.2. The built geometry is visualized in Figure 3.12: a palladium layer of thickness 500 nm, followed by a 350 nm MgH_2 layer and then by a 500 nm Mg layer. Grains in the hydride layer were represented as hexagons, surrounded by a 1 nm thick grain boundary. The grain diameter is represented here by the distance between opposite vertices of the hexagon. The simulations were performed for grain sizes of $d = 100\text{ nm}$, $1\text{ }\mu\text{m}$, $10\text{ }\mu\text{m}$ and $100\text{ }\mu\text{m}$. The corresponding grain boundary concentrations in the hydride layer are respectively 4%, 0.4%, 0.04% and 0.004%. The geometry was modified for larger grain sizes by keeping the same thickness of the Mg, MgH_2 and Pd layers and adjusting the vertical dimension to $4 \cdot d$, as shown in Figure 3.13 for $d = 1\text{ }\mu\text{m}$.

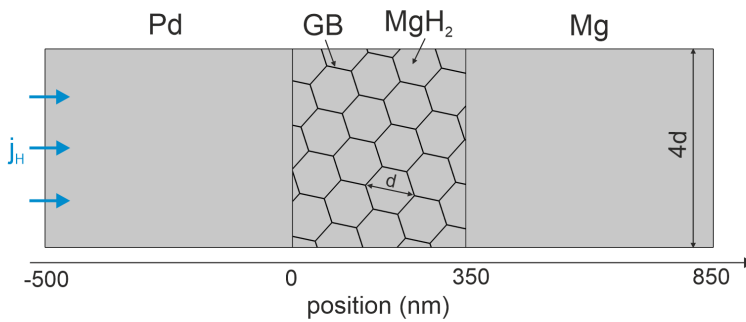


Figure 3.12: Geometry for the FEM diffusion simulation for a grain size of $d = 100\text{ nm}$. Similarly to electrochemical loading experiments, hydrogen is introduced from the palladium surface and then has to diffuse through a MgH_2 blocking layer which also contains grain boundaries.

Although diffusion is a tridimensional process, the geometry could be simplified to a bidimensional section. This is possible because hydrogen diffusion happens against the concentration gradient according to Fick's laws (see section 2.3.6). Since hydrogen is loaded from the entire Pd surface, the resulting hydrogen concentration is uniform on planes parallel to the sample's surface, meaning that the concentration gradient is different from zero only in the direction perpendicular to the surface. Therefore, diffusion will be observed only in the direction perpendicular to the sample's surface. In the absence of grain boundaries, a linear simulation already describes the process. To include grain boundaries, it is sufficient to simulate a plane perpendicular to the Pd surface and assume that parallel planes will behave similarly. This choice simplifies the domain

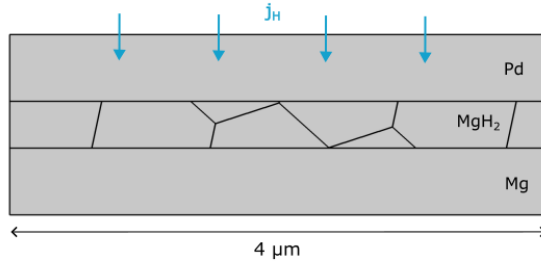


Figure 3.13: Geometry for the FEM diffusion simulation for a grain size of $d = 1 \mu\text{m}$. While the thickness of the Pd, Mg hydride and Mg layers is the same as for the grain diameter of 100 nm (Figure 3.12), the lateral extension is increased to match the grain size, reaching a value of $4 \cdot d = 4 \mu\text{m}$.

geometry, strongly improving the computation efficiency. Always with the objective of simplifying geometry, grain boundaries were only included in the magnesium hydride domain, and not in the $\alpha\text{-Mg}$ and $\alpha\text{-Pd}$ portions of the model. This choice is justified by the already fast hydrogen diffusion coefficients for H in $\alpha\text{-Mg}$ and $\alpha\text{-Pd}$ (see section 2.3.6), for which grain boundaries are not expected to lead to faster overall hydrogen diffusion. Moreover, diffusion through MgH_2 constitutes almost the entirety of the diffusion time, so that even improved transport through the Pd and Mg layers would not affect the global results of the simulation.

The simulation consisted of two steps. First, a hydrogen flux of $8.25 \times 10^{-6} \text{ mol}/(\text{m}^2\text{s})$ was applied at the Pd surface for 90 s (blue arrows in Figures 3.12 and 3.13). This corresponds to a current density of $80 \mu\text{A}/\text{cm}^2$, and therefore mimics the loading step during electrochemical loading (see section 3.4). As a consequence, the hydrogen concentration in the Pd layer increases. Then, the incoming hydrogen flux is set to 0, and hydrogen diffuses from this initial distribution into the MgH_2 and Mg layers. This mimics the waiting interval during electrochemical loading. The hydrogen concentration is evaluated every 30 minutes for 30 hours, by calculating line averages for positions between -100 nm and 450 nm with a 50 nm spacing. The total simulation time was 842 s, of which 652 s were necessary for the larger grain size of $d = 100 \mu\text{m}$.

The mesh for the study was obtained through adaptive mesh refinement using the general modification adaptation method during the second simulation step. The starting mesh for the adaptive refinement was a custom free triangular mesh with the following parameters: maximum element size 30 nm, minimum element size 0.8 nm, maximum element growth rate 1.1, curvature factor 0.2. As an example, the resulting mesh after adaptive refinement for $d = 100 \text{ nm}$ is reported in Figure 3.14.

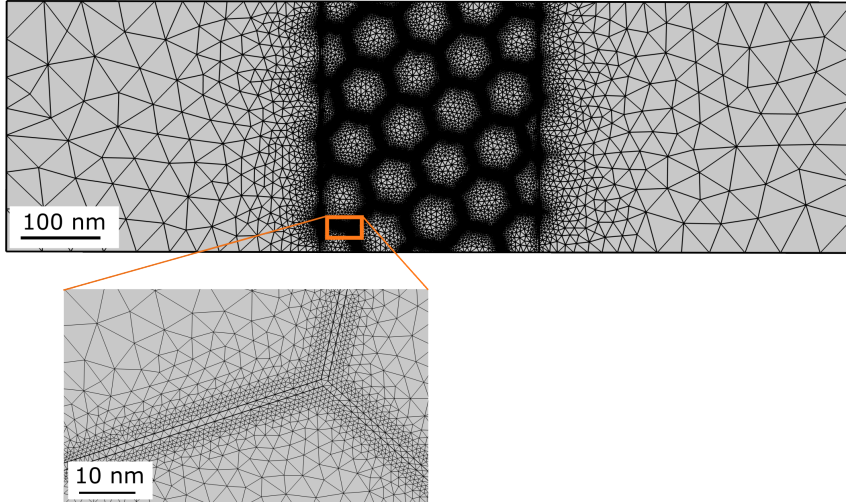


Figure 3.14: Results of the adaptive mesh refinement for $d = 100\text{ nm}$. The smallest mesh elements are located at the interface between the different materials, and between grains and grain boundaries in the MgH_2 domain.

The quality of the mesh can be evaluated by geometric parameters such as the skewness (S), which measures the deviation of the triangular elements of the mesh from an ideal element consisting of an equilateral triangle. In general the skewness is defined as:

$$S = 1 - \max \left(\frac{\theta - \theta_e}{180^\circ - \theta_e}, \frac{\theta_e - \theta}{\theta_e} \right) \quad (3.11)$$

where θ is the angle over a mesh vertex and $\theta_e = 60^\circ$ is the angle of an ideal element (equilateral triangle). The skewness of the ideal mesh element, for which $\theta = \theta_e$, is therefore $S = 1$. An average value close to $S = 1$ indicates a high quality mesh, where the elements are not excessively deformed or inverted. In the simulation, an average value of $S = 0.88$ was achieved, with a minimum skewness of 0.48. Moreover, during adaptive mesh refinement the element size in different areas is varied to reach a compromise between precision and simulation time. This is achieved by gradually reducing the mesh size while computing the difference in calculated concentration, until a convergence is reached.

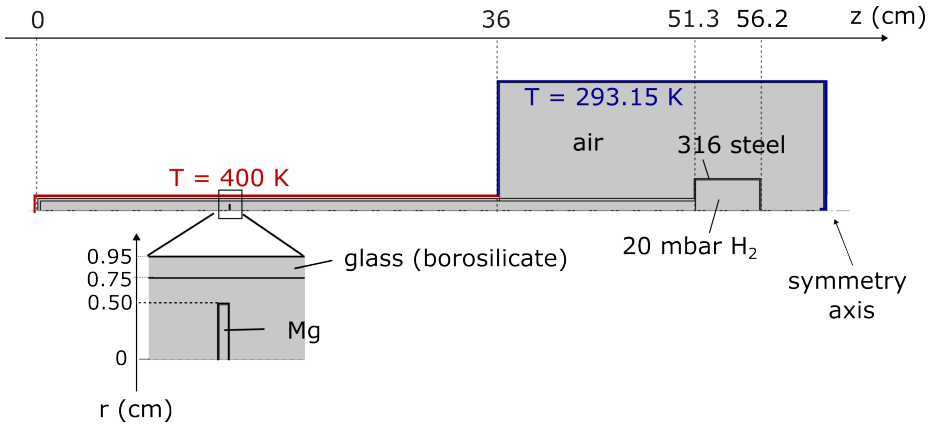
Table 3.4 reports the simulation parameters for H diffusivity and concentration. The concentration in the Pd layer was chosen so that the equilibrium surface potential would match that of Mg hydride, according to the isotherms for Pd thin films in Wagner et al. [21]. The diffusion coefficients are chosen based on the expected values at grain boundaries and inside the grains at room temperature, as introduced in section 2.3.6.

Table 3.4: Simulation parameters for the different domains (initial H concentration and H diffusion coefficient).

Domain	c_H^0 (mol/m ³)	D_H (m ² /s)
Pd	1017	3×10^{-11}
MgH ₂ grains	0	1×10^{-28}
MgH ₂ GBs	0	1×10^{-16}
Mg	0	1×10^{-11}

3.6.2 Heat transport during gas volumetry at 398.2 K

FEM simulations were also performed to understand the temperature evolution in the experimental setup and in Mg samples during gas loading at 398.2 K. Figure 3.15 represent the simulation geometry, based on the setup described in section 3.5.2. As in the experimental setup, the temperature variation due to heating was studied for a borosilicate glass filled with 20 mbar of hydrogen gas. The geometry of the glass tube coincides with the real counterpart in the experiment. Attached to the glass tube was a steel container of the same volume of chamber 1 in Figure 3.9. A radial symmetry was used during the simulation, so that only a surface going from the center of the system to its outside radius has to be studied. Moreover, a Mg discs with the same geometry as the samples described in section 3.1 was added to the simulation.

**Figure 3.15:** Geometry for the heat transport FEM simulation. The geometry represents the experimental setup described in section 3.5.2.

To mimic the effect of the oven, the external temperature of the glass tube was fixed to 400 K for a length of 36 cm. To represent cooling in the system parts outside the oven, an air volume was added around the surfaces not in contact with the oven, and the temperature at its border was set to room temperature (293.15 K). Doing so, the cooling rate is not limited by the air volume

available in the simulation and the geometry represents cooling in a much larger environment, like the laboratory where the real system is located. In the rest of the simulated area, the initial temperature was set to 293.15 K and then left free to change.

Heat transport was simulated using the *Heat Transfer in Solids and Fluids* module of Comsol Multiphysics 6.2, which includes heat transfer by radiation, convection and conduction. For this study, a free triangular mesh with the following parameters was used: maximum element size 6.13 mm, minimum element size 0.0123 mm, maximum element growth rate 1.1, curvature factor 0.2. The skewness as defined in Eq. 3.11 had an average values of 0.87 and a minimum value of 0.40. Two main issues regarding the loading experiment were addressed by two different simulations. Firstly, how much time is required so that the Mg sample and the surrounding hydrogen gas achieve thermal equilibrium with the outside wall of the glass tube. Secondly, how does the temperature of the hydrogen gas outside of the oven vary during the loading experiment. The real simulation time was 7 s for the first study and 4 s for the second study.

To answer the first question, a time dependent study was performed, analyzing the temperature distribution at intervals of 0.1 min for a total of 30 min. From this data, the temperature evolution at the center of the Mg sample thickness (at $r = 0$) was plotted over time and compared with the temperature evolution of the H_2 gas 5 cm above the Mg sample (also at $r = 0$). Figure 3.16 shows the temperature profile along the symmetry axis of the glass tube during the first 30 min of heating. It can be seen that the hydrogen gas inside the oven reaches the temperature of 400 K after a few time steps (approximately 30 s). The temperature of the magnesium sample and of the gas in its vicinity also gradually increases until it reaches 400 K, but requires a higher number of steps, with a duration of about 60 s. The temperature evolution of the Mg sample and of the 20 mbar H_2 gas at a distance of 5 cm from the Mg disc are plotted in more detail in Figure 3.17. Both elements have an initial temperature of 293.15 K. The temperature is set to 400 K on the outside surface of the borosilicate tube containing the gas and the sample. After less than 0.5 min, the H_2 gas reaches a stable temperature of 400 K. The temperature increase is slightly slower for the Mg sample, which however reaches 400 K after less than 1 min. These times are short compared to the duration of the loading experiment, where hydrogen is absorbed over a span of ~ 8 h. Therefore, we can consider the temperature of the hydrogen gas and of the Mg sample to be constant and equal to 400 K during the loading experiment described in section 3.5.2. Outside of the oven, as can be seen in Figure 3.16, the temperature gradually drops to the initial value of 293.15 K. The transition zone extends roughly until the end of the glass tube, and its temperature increases gradually over time.

To answer the second question, a temperature profile along the symmetry axis ($r = 0$) was plotted, representing the temperature variation along the z-axis at different times. For a more long-term consideration, a second time dependent study was performed, looking at the temperature distribution at intervals of 30 min for a total of 8 h. The obtained temperature profile is plotted in Figure

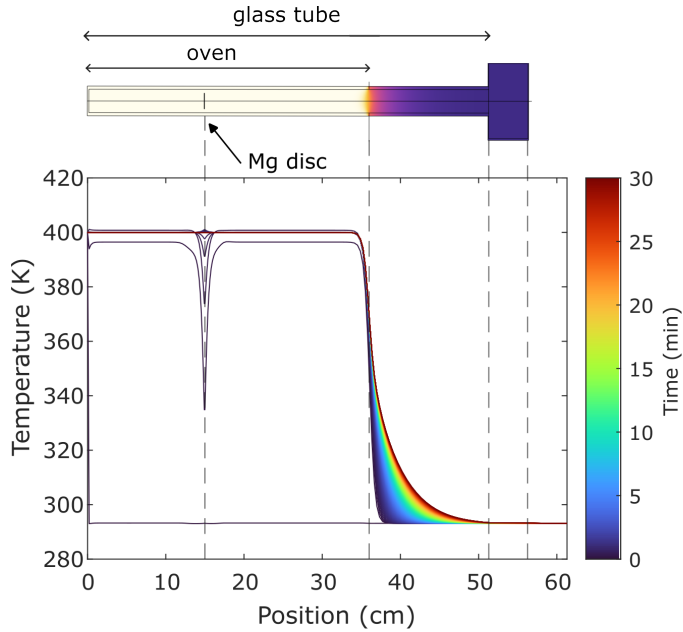


Figure 3.16: Temperature profile in the vacuum system during hydrogen loading, plotted at intervals of 6 s for 30 min. The temperature on the exterior surface of the glass tube was set to 400 K for the first 36 cm. The representation has been enlarged in the radial direction to improve visibility. The temperature quickly reaches 400 K inside the oven and declines gradually to room temperature outside of it. The extension of the transition zone increases with time.

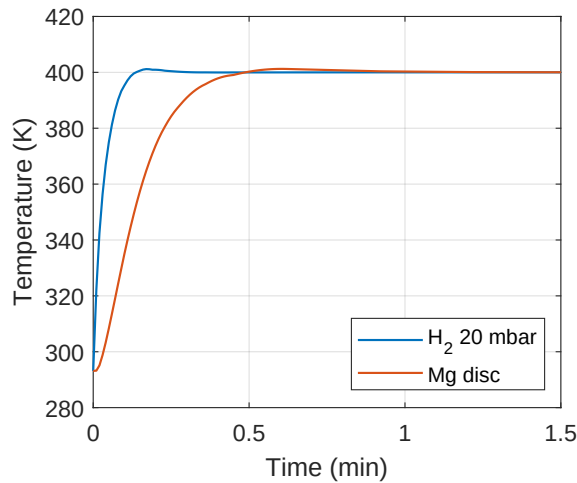


Figure 3.17: Temperature variation at center of the Mg sample and for the H_2 gas at the center of the gas tube, 5 cm above the magnesium sample, during the first 1.5 min of heating. Both the hydrogen gas and the Mg disc reach the goal temperature of 400 K less than one minute after starting the oven.

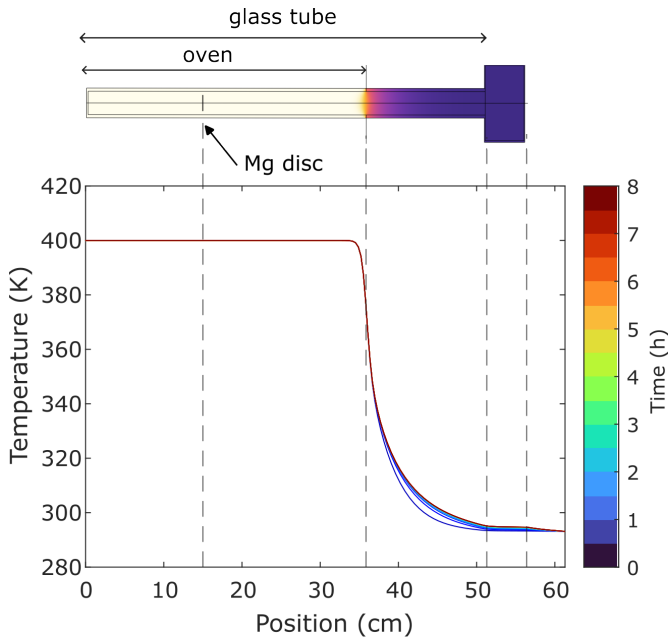


Figure 3.18: Temperature profile in the vacuum system during hydrogen loading, plotted at intervals of 30 min for 8 h. The temperature on the exterior surface of the glass tube was set to 400 K for the first 36 cm. The representation has been enlarged in the radial direction to improve visibility. The temperature is stable inside the oven and decreases gradually outside of it. In the furthest volume from the oven a temperature increase lower than one degree is observed over 8 h.

3.18 for the first 8 h of loading at intervals of 30 min. The temperature in the heated portion of the setup is stable at 400 K, outside of the oven the temperature drops to a stable value close to room temperature in the steel portion of the loading chamber. Here, a temperature variation of ~ 1 K is observed over a period of 8 h due to heat transport from the part of the experimental setup contained in the oven, despite heat dissipation in air being included in the model for the setup parts outside of the oven (see section 3.6.2). A variation of 1 K over 8 h for the setup volume outside of the oven is quite small, for example in comparison to oscillations of the temperature of the room where the experiment was performed. Regarding the transition zone, extending until the end of the glass tube, its temperature varies over time. However, the largest variation is observed in the first hour, and a constant profile is achieved after roughly 4 h.

In the loading experiment (section 3.5.2), the pressure variation during hydrogen absorption is measured in the steel chamber with a larger diameter compared to the glass tube. Here, no relevant increase of the gas temperature above room temperature is expected according to the simulation. Therefore, we can assume that the measured pressure depends only on hydrogen absorption and not on temperature increases due to heat transport from the heated parts of the systems. In fact, the temperature change of one degree over 8 hours would introduce a negligible

error to the measured hydrogen pressure. To associate the measured pressure variation to the amount of absorbed or released hydrogen gas with Equation 3.10, we however need to know the temperature within the whole experimental setup. The equation was derived to describe a closed system with two distinct temperatures, because calculating the amount of absorbed hydrogen with a single temperature would introduce a systematic error, as shown in Figure 3.10. This only approximates the temperature distribution in the experimental setup emerging from this simulation. In fact, while the temperatures in the oven and in the steel container where the pressure is measured are uniform and do not vary strongly with time, the temperature in the transition zone increases with time and depends on the distance from the oven's opening. This must be considered when evaluating the experimental results. A very conservative estimate, giving a lower limit to the amount of absorbed gas, is given by considering the whole transition zone to have a temperature of 400 K. This was taken as the lower limit for the calculated n_{abs} (see section 3.5.2, Figure 3.10). The upper limit was calculated assuming that the whole transition zone is at room temperature.

3.7 Positron Annihilation Spectroscopy (PAS)

Positron annihilation spectroscopy is a non-destructive experimental technique which allows to study the electronic structure, the presence of lattice defects and the chemical composition of samples by measuring the lifetime of absorbed positrons and the momentum distribution of emitted photons. This technique was used in this work to measure the dislocation density resulting from HPT of ZK60 samples. Moreover, coincidence doppler broadening was employed to characterize the chemical environment of dislocations in HPT-deformed ZK60. The experimental results are reported in section 4.6. This section introduces the experimental technique and the setup used in this work.

When positrons enter a solid, their energy quickly diminishes by interacting with the charged ion cores and electrons, until they reach thermal equilibrium with the environment [193]. After thermalization, the distribution of positrons in a perfect crystal lattice can be approximated as uniform, excluding the areas near the atoms' ion cores [193]. Therefore, positrons are delocalized and occupy with the same probability the interstitial regions of the crystal lattice; these positrons are described as free or quasi-free [193, 194]. Open-volume defects can provide localized bound states for positrons due to the lower repulsion from the ion cores [193], leading to trapping of the positrons if the energy is low enough compared to the value in the interstitial sites.

Finally, positrons annihilate by interacting with an electron. This process involves the emission of one to three photons [194]. However, the two-photon emission process is the most frequent with a cross section two orders of magnitude larger than the three-photon process and eight orders

of magnitude larger than the one-photon emission process [194]. For the two-photon process at low positron velocity, the positron annihilation probability in a material is given by [194]:

$$\Gamma = \pi r_0^2 c n_e \quad (3.12)$$

where r_0 is the classical electron radius, c is the speed of light and n_e is the local electronic density. Therefore, the annihilation probability directly depends on the electronics density near the positron.

The following paragraphs describe how positron annihilation can be described in the case of a single trapping state and how the chemical environment affects the positrons' momentum distribution.

3.7.1 The two-state simple trapping model

The two-state simple trapping model (STM) describes the annihilation of positrons in a solid where two states are available. The first state, which is also assumed as the initial state at $t = 0$ [195], usually describes delocalized positrons in the interstitial sites of a crystalline solid, while the second state describes positrons trapped in a localized state created by defects in the crystal structure.

The time evolution of the number of positrons in the two states is given by [193, 194]:

$$\frac{dn_f}{dt} = -\lambda_f n_f - k n_f \quad (3.13)$$

$$\frac{dn_t}{dt} = -\lambda_t n_t + k n_f \quad (3.14)$$

where n_f describes the number of free positrons in the delocalized state, while n_t is the number of positrons trapped at defects. The annihilation rate is described by $\lambda_f = 1/\tau_f$ for quasi free positrons and by $\lambda_t = 1/\tau_t$ for trapped positron. k is the trapping rate, describing the frequency at which positrons move from the free to the trapped state. The trapping rate can further be expressed as $k = v_d \rho_d$, where v_d is the trapping rate for a single defect and ρ_d is the defects concentration.

Equations 3.13 and 3.14 imply that the number of free positrons decreases either by annihilation or by trapping, while the number of trapped positrons decreases only by annihilation. Therefore, detrapping of the positrons is not included in the model. Moreover, the model assumes capture-limited trapping, and a uniform spatial distribution of defects.

When two different states are available, two different lifetimes τ_1 and τ_2 can be observed in the annihilation spectrum, with different intensities I_1 and I_2 . The global annihilation rate dN/dt is given by [194, 195]:

$$\frac{dN}{dt} = -N_0 \left(\frac{I_1}{\tau_1} e^{-t/\tau_1} + \frac{I_2}{\tau_2} e^{-t/\tau_2} \right) \quad (3.15)$$

where N_0 is the initial number of positrons in the sample and the intensities are normalized so that $I_1 + I_2 = 1$.

The effective lifetimes τ_1 and τ_2 and intensities I_1 and I_2 can be determined experimentally from emission spectra, and can be related to the lifetimes of free and trapped positrons τ_f and τ_t . In particular, $\tau_2 = \tau_t$ [194, 195], meaning that the lifetime of trapped positrons can be directly determined from the emission spectra. For τ_f we have [194, 195]:

$$\lambda_f = \frac{1}{\tau_f} = \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \quad (3.16)$$

In cases where τ_f is a well-known value, Eq. 3.16 can be used to validate the use of the simple two-state model in the description of experimental data.

Finally, the defects density ρ_d can be calculated as [193]:

$$\rho_d = \frac{I_2}{v_d} \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \quad (3.17)$$

if the trapping frequency v_d is known for the specific material and type of defect. This equation allows to extract the density of defects from experimental lifetime spectra.

3.7.2 Doppler Broadening during positron annihilation

Together with lifetimes measurements, the electronic density in the solid can also be characterized through the energy of the emitted photons. If we consider the frame of reference of the center of mass of the electron-positron pair, the two photons must be emitted in opposite directions to conserve the total momentum of the system. They each have an energy which is half of the total energy of the system [194]:

$$E_{tot}^{CM} = 2m_0c^2 - E_B \quad (3.18)$$

where m_0c^2 is the rest mass of the electron and E_B is the electron binding energy.

In the laboratory frame of reference, due to the non-zero momentum of electrons and positrons, the total energy of the system is [196]:

$$E_{tot} = \sqrt{m_0^2 c^4 + p_{e^-}^2 c^2} + \sqrt{m_0^2 c^4 + p_{e^+}^2 c^2} - E_B \quad (3.19)$$

where p_{e^-} and p_{e^+} is the momentum of respectively the electrons and the positrons. After the thermalization process, the momentum of the positron is much lower than that of the electron ($p_{e^+} \ll p_{e^-}$). If we further assume that $p_{e^-} \ll m_0 c^2$, the energies of the two annihilation photons are [194, 196]:

$$E_1 = m_0 c^2 + \frac{p_L c}{2} - \frac{E_B}{2} \quad (3.20)$$

$$E_2 = m_0 c^2 - \frac{p_L c}{2} - \frac{E_B}{2} \quad (3.21)$$

where p_L is the momentum of the electron along the emission direction of the photons (longitudinal momentum). Therefore, the measured photon energy will present a Doppler shift $\Delta E = p_L c/2$ with respect to $m_0 c^2$. Considering the signals of a high number of annihilation events, the photon energy will be centered around $m_0 c^2$, with a Doppler broadening related to the distribution of the electrons' longitudinal momentum p_L . Therefore, the measured doppler broadening carries information on the momentum distribution of the electrons in the solid.

The coincidence Doppler broadening (CDB) technique, introduced by Lynn et al. [197], is based on the simultaneous determination of the energy of both annihilation photons. For thermalized positrons we then have:

$$E_1 + E_2 = 2m_0 c^2 - E_B \quad (3.22)$$

$$E_1 - E_2 = p_L c \quad (3.23)$$

This technique reduces the background signal and allows to observe the high-momentum tails of the annihilation peak. This signal comes from positrons interacting with high-momentum core electrons, whose energy is not affected by crystal bonding. Therefore, CDB is suitable for the chemical analysis of positron annihilation sites.

3.7.3 PAS experimental parameters

Positron Annihilation Spectroscopy (PAS) measurements and analysis were performed in collaboration with Prof. Jakub Čížek at Charles University in Prague, Czechia.

A ^{22}Na radioisotope with an activity of 1 MBq was utilized as positron source. This positron source was sealed between Kapton foils with a thickness of 7.5 μm , and the diameter of the

positron source spot was approximately 1 mm. During measurements, the positron source was sandwiched between two pieces of the measured sample.

Positron lifetime measurements were conducted using a digital spectrometer [198] with a time resolution of 145 ps (FWHM of the resolution function). A minimum of 10^7 positron annihilation events were collected for the positron lifetime spectrum of each sample. The decomposition of positron lifetime spectra into individual components was performed using the PLRF code [199]. The source contribution, determined using the procedure described in Ref. [200], was always subtracted from positron lifetime spectra.

Coincidence Doppler broadening (CDB) spectroscopy was employed to characterize the local chemical environment of the positron annihilation sites. CDB investigations were conducted with a digital CDB spectrometer with two HPGe detectors, achieving a net energy resolution of 0.99 keV at 511 keV [196]. Each CDB spectrum accumulated at least 10^8 positron annihilation events, and the peak-to-background ratio for the annihilation photo-peak exceeded 10^5 . The results of the CDB investigations are presented as ratio curves related to a well-annealed pure Al reference with a purity of 99.9999%.

Since in torsion deformation strain increases with radial distance r from the center of the sample disc (see section 3.1.3), positron annihilation measurements of HPT-deformed samples were performed at $r = 0, 1.5$, and 3 mm from the center of the sample by positioning the center of the positron source spot accordingly.

3.8 HPT-deformation and characterization of Mg samples below 223 K

As introduced in section 2.3.9, high-pressure torsion on pure Mg reduces the average grain size down to $\sim 1 \mu\text{m}$. However, it was not yet shown whether an even smaller grain size could be observed by deforming and characterizing the samples at lower temperatures. By decreasing the working temperature, we expect a reduced mobility of the grain boundaries, which would lead to an overall finer microstructure as introduced in section 2.2.5. To check this hypothesis, the samples must be deformed at cryogenics temperatures. The low temperature then has to be maintained until the sample's microstructure has been characterized, since even a short exposure to higher temperatures could alter the microstructure, nullifying the effect of the previous cryogenic treatment.

This aspect was investigated in collaboration with Ms. Xiaomeng Fan and Dr. Sabine Schlabach, as a part of Ms. Fan's Master Thesis. A cold chain was implemented, bringing the samples from

Table 3.5: Processing conditions of Mg samples

Sample name	Pressure	No. of rotations	Rotation speed	HPT temperature
Mg-5G-N2-RT	5 GPa	2	1 rpm	RT
Mg-5G-N7-RT	5 GPa	7	1 rpm	RT
Mg-5G-N5-LN	5 GPa	5	1 rpm	LN
Mg-5G-N7-LN	5 GPa	7	1 rpm	LN

deformation in the HPT machine to characterization in the SEM. More details about each step are reported in the following:

- **HPT deformation:** Severe plastic deformation of the sample happens in an HPT machine. During the process the sample is cooled with Liquid Nitrogen (LN), achieving a temperature of 77 K.
- **Storage:** Between deformation and characterization the sample is stored in a Liquid Nitrogen dewar, therefore maintaining the temperature of 77 K.
- **Transfer:** To characterize its microstructure, the sample must be mounted on a suitable sample holder and transferred into the vacuum chamber of the SEM. To do so, the sample holder is pre-cooled in dry ice achieving a temperature of 194.7 K. The sample is then mounted on the holder, always while cooling with dry ice.
- **Characterization:** The sample's microstructure is characterized in the SEM. Here the temperature is controlled using a Deben cryostage, whose temperature is set at the lowest value of 223 K. The surface to be characterized is directly prepared in the SEM vacuum chamber to reduce Magnesium oxide and hydroxide formation.

The Ga-ion beam (FIB) available at the SEM was used to remove part of the material and create a high-quality cross-section perpendicular to the sample's surface (see also section 3.2.1. This method has the advantage that the surface to be characterized is created directly in vacuum conditions ($\sim 10^{-6}$ mbar), thus reducing oxide and hydroxide formation. The samples were then imaged by SE contrast in the SEM, and the grain size distribution was analyzed similarly to how introduced in section 3.2.1. The samples were deformed according to the parameters in Table 3.5. Figure 3.19 shows the resulting average grain size for samples treated according to the cold chain and samples deformed and characterized at room temperature.

It emerges that the treatment according to the cold chain does not significantly affect the resulting grain size. This might be due to the insufficiently low temperature achievable with the cryostage.

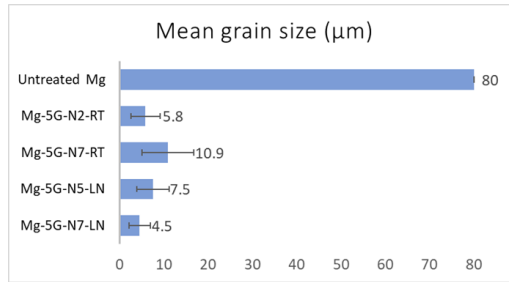


Figure 3.19: Resulting grain size for Mg samples deformed and characterized according to the cool chain and at room temperature, in comparison with undeformed magnesium.

4 Results

To analyze the direct influence of grain boundaries on hydride formation in Mg and Mg-alloys several aspects have to be considered. The fraction of grain boundaries has to be high enough to contribute to the measured effective diffusion. In this work, this was achieved by reducing the average grain size of Mg and ZK60 samples using HPT. However, besides increasing the GBs concentration, this method also introduces other types of defects, such as dislocations. Moreover, the different chemical compositions of Mg and ZK60, and especially the intermetallic phases present in ZK60, can also affect hydrogen absorption. Therefore, the first step in understanding the role of grain boundaries is characterizing the microstructure of Mg and ZK60 samples before and after HPT deformation, as presented in sections 4.1 and 4.2. Afterwards, section 4.3 presents the results of room-temperature electrochemical loading for magnesium and ZK60 samples before and after HPT. Effects of the samples' chemical composition and microstructure are observed, together with effects related to the chosen loading parameters. Section 4.4 deals with FEM simulations of grain boundary hydrogen diffusion through magnesium hydride, contributing to the interpretation of electrochemical loading results. Section 4.5 reports the result from gas-phase hydrogen loading. These experiments were performed at room temperature and at 398.2 K, to observe further microstructure effects on hydrogen absorption and their variation with the loading temperature. Section 4.6 reports the PAS results, which allow to calculate the dislocation density resulting in ZK60 after HPT. Finally, section 4.7 reports the results of in-situ TEM hydrogen loading in ZK60 at room temperature and at 398.2 K, allowing to observe the time evolution of hydride formation and the resulting microstructure after hydrogen desorption.

4.1 Microstructure characterization of as-extruded and HPT-deformed discs

The microstructure evolution of the studied samples following HPT deformation is described in this section. Results related to pure Mg samples are reported in section 4.1.1, while results related to ZK60 are reported in section 4.1.2. Finally, section 4.1.3 deals with quantifying the grain size distribution for the different samples in different deformation states.

4.1.1 Mg discs before and after HPT-deformation

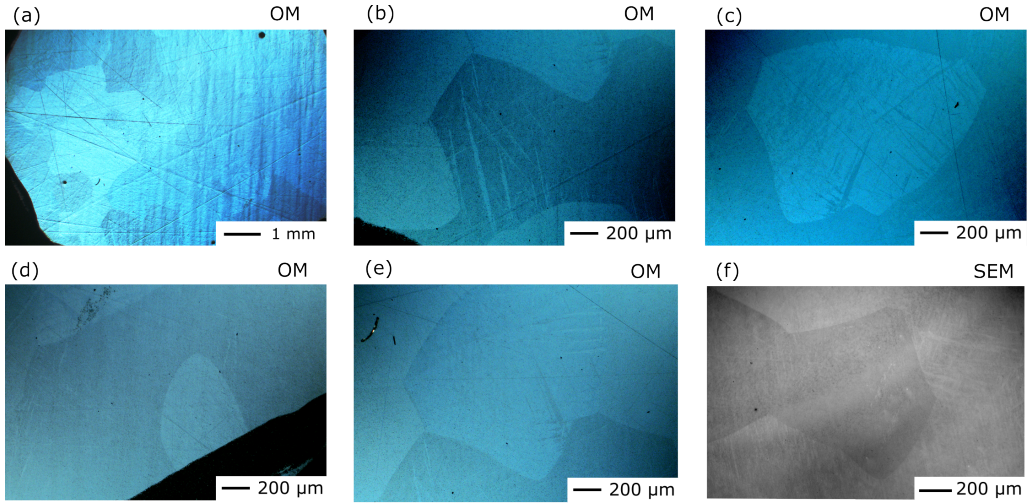


Figure 4.1: Images of the surface of undeformed Mg samples: (a) to (e) using a optical microscope (OM) with polarized light and (f) with the SEM InLens detector. The grains are very coarse, with sizes in the mm range.

The microstructure of Mg discs was characterized in the as-extruded state and after HPT deformation. Figure 4.1 shows optical microscopy (OM) images of the surface of Mg discs before plastic deformation. Surface characterization was performed for Mg discs without the Pd coating necessary for H absorption, therefore these surface images describe the properties of pure Mg. The grains visible on the surface are extremely coarse, with sizes close to 1 mm. Therefore, they can be observed using an optical microscope with polarized light after the metallographic preparation described in section 3.2. Grains of similar size were also observed in the SEM, as Figure 4.1.f shows. Several scratches are visible in these low-magnification images, especially in Figure 4.2.a, resulting from the difficulties of metallographic preparation for large Mg surfaces as described in section 3.2.1. Moreover, OM with polarized light tends to enhance topographical contrast, highlighting scratches and irregularities on the surface.

The microstructure resulting after HPT-deformation is shown in Figure 4.2 at different resolutions and at different positions across the sample's radius. As visible in Figure 4.2.a and 4.2.b, the grains at the sample's center are less regular in shape and size compared to the grains at $r \sim 2.5$ mm. For $r = 0$, grains larger than $1 \mu\text{m}$ are visible, surrounded by smaller grains, while at the sample's mid-radius (2.5 mm) the grains appear more regular. A more detailed analysis of the grain size is reported in section 4.1.3.

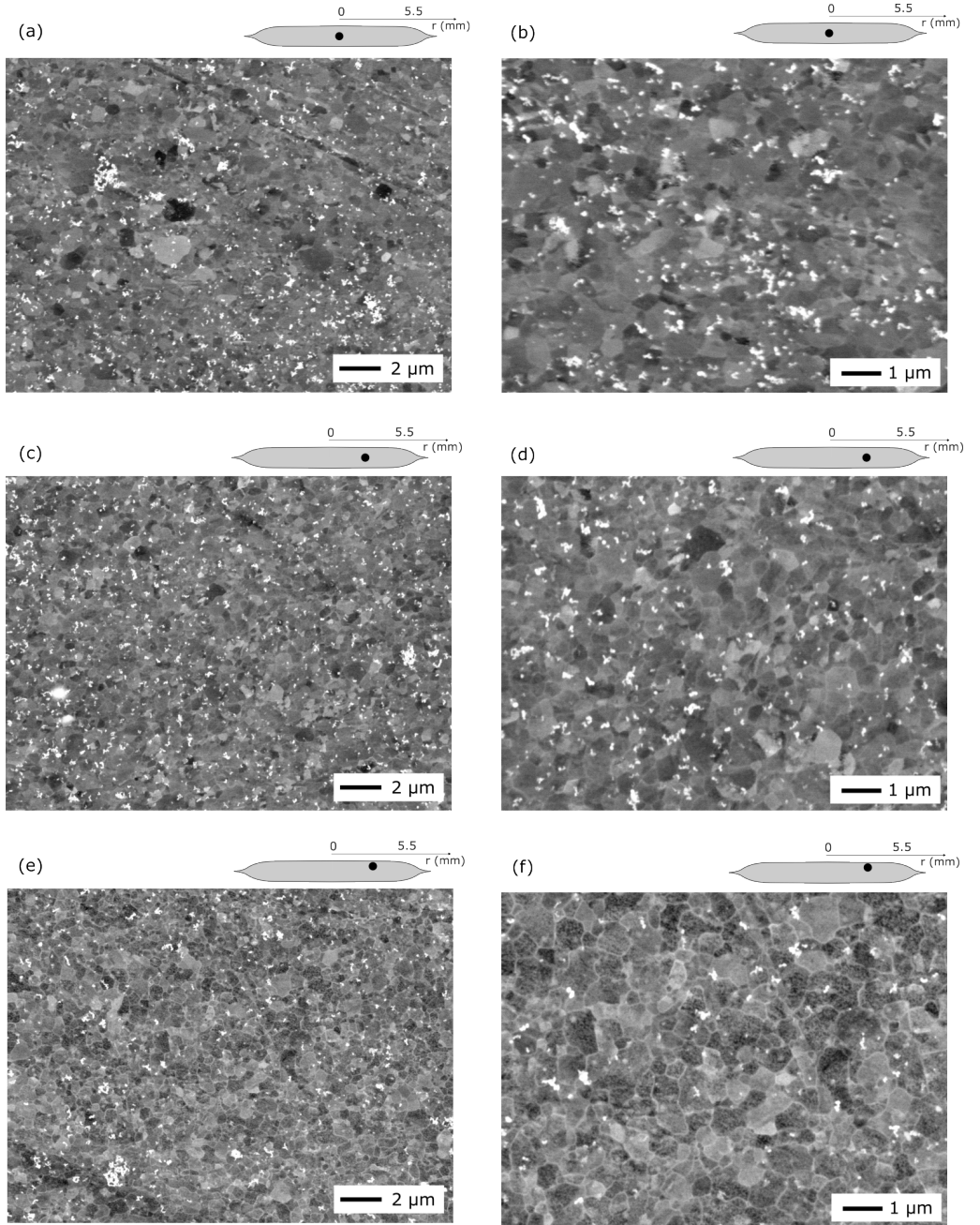


Figure 4.2: SEM micrographs using BSE contrast for the cross-section of one HPT-deformed Mg sample at two different resolutions. The images are taken close to the sample center for (a) and (b), at $r \sim 2.5$ mm in the middle of the disc for (c) and (d), and at $r \sim 2.5$ mm close to the sample's surface for (e) and (f). The grain size is below $1 \mu\text{m}$, variations are observed across the radius and depending on the distance from the sample's surface.

The sample was also observed at the mid-radius close to its surface, as shown in Figure 4.2.e and 4.2.f. Here, while the grain size does not appear different from what observed at the sample's center, the grain boundaries are more strongly visible and some contrast appears within the grains. The white spots visible on the surface are also further analyzed in section 4.1.2.

4.1.2 ZK60 discs before and after HPT-deformation

The microstructure of ZK60 samples was characterized before and after HPT by SEM imaging and EDS, as described in section 3.2. Both the surface and the cross-section of ZK60 discs were studied. As for pure Mg discs, the surface was studied without Pd coating. Discs used for hydrogen loading experiments were cut from extruded rods. For undeformed samples, the surface of the cut discs is perpendicular to the extrusion direction (see Figure 3.2), while the cross section is parallel to it. For the HPT-samples the disc surface is perpendicular to both the extrusion direction and the HPT rotation axis.

Figure 4.3 shows images of the discs' surface at different length scales and positions for undeformed and HPT-deformed ZK60. The discs were observed at two positions: close to the center and close to the edge. Figure 4.3.a-f shows surface images of an undeformed ZK60 sample. At the highest magnifications (20 and 10 μm scale bars), alternating dark and bright bands are visible, both at the sample's center (Figure 4.3.a and 4.3.b) and at its edge (Figure 4.3.d and 4.3.e). At higher magnification (Figure 4.3.c and 4.3.f), it appears that the bright bands are formed by a high density of small bright precipitates, which are less dense in the dark bands. Some larger bright particles with sizes close to 1 μm are also visible in Figure 4.3.b and 4.3.e. The composition of these larger particles was investigated in the materials' cross section, as reported later in this section. Regarding the small precipitates, their composition was investigated by TEM in section 4.7. The microstructure of HPT-deformed samples is shown in Figure 4.3.g-l. Similarly to the undeformed samples, alternating bright and dark bands are visible, which are characterized respectively by low and high densities of bright precipitates. Larger precipitates of size close to 1 μm are also visible, similarly to the undeformed samples.

The cross-section of both undeformed and HPT-deformed samples was also observed by BSE contrast. Figure 4.4 shows the cross-section of one undeformed ZK60 disc at different magnifications close to the center (Figure 4.4.a-c) and to its edge (Figure 4.4.d-f). Here, the alternating small precipitates bands are visible as vertical stripes, and their appearance does not differ between center and edge of the sample. Larger bright precipitates of size close to 1 μm are also visible, and are arranged in vertical chains (see Figure 4.4.b and 4.4.e). Grains of sizes between 5 μm and 10 μm can be seen in the images – a more detailed analysis of the grain size is reported in section 4.1.3. Also regarding the grain size, there is no strong difference between the

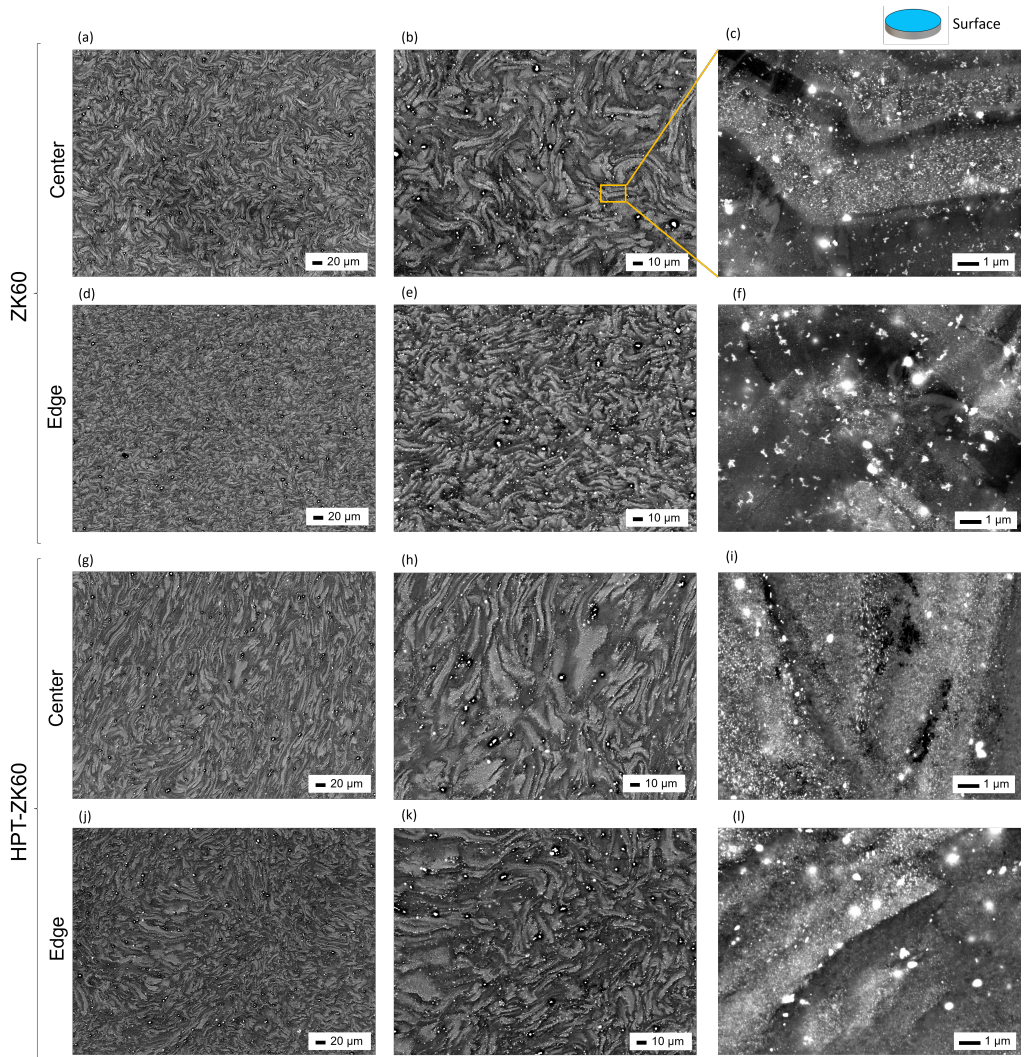


Figure 4.3: Surface SEM micrographs of undeformed ZK60 samples at different length scales close to the disc center (a)-(c) and to its edge (d)-(f), and of HPT-deformed ZK60 samples close to the disc center (g)-(i) and to its edge (j)-(l). The images are obtained using backscattered electrons contrast (BSE) and refer to the surface of the disc samples, perpendicular to the extrusion direction (see also Figure 3.2). Bright bands characterized by a high concentration of bright precipitates can be seen with a similar structure for undeformed and HPT-deformed samples across different positions along the sample's radius.

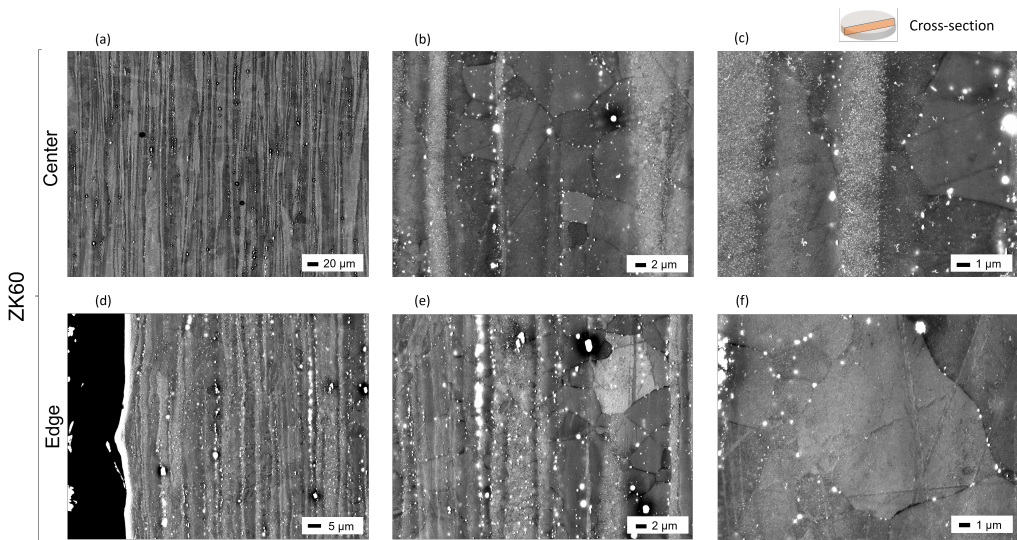


Figure 4.4: SEM micrographs of undeformed ZK60 samples at different length scales close to the disc center (a)-(c) and to its edge (d)-(f). The images are obtained using backscattered electrons contrast (BSE) and refer to the cross-section of the disc samples, perpendicular to the extrusion direction (see also Figure 3.2). Bands of bright particles parallel to the extrusion direction are visible at different position across the radius, together with larger particles in the μm range. The visible grains are several micrometer large and bright precipitates decorate their grain boundaries.

center and the edge of the disc. In all positions, the grain boundaries are decorated with bright precipitates.

Some of the larger bright particles have been characterized by EDS, as shown in Figure 4.5. The EDS spectrum with peak identification is reported in Figure 4.5.b, while the spatial distribution of the identified elements is reported in Figure 4.5.c-h. The particles show a depletion of Mg and an enrichment of the alloying elements Zn and Zr, and can therefore be associated to intermetallic phases such as Zn_2Zr , which are expected in ZK60 according to the phase diagram in Figure 2.2. Moreover, the Zn-Zr precipitates show an increased content of contaminants such as carbon and oxygen, together with an increased silicon content.

Since the samples do not originally contain Si or C, the contamination with C, O and Si is likely caused by the metallographic preparation as introduced in section 3.2; in particular, silicon is present in the solution used for the last polishing step. It must be noted that some bright structures visible in Figure 4.5.a on the right side of the Zn-Zr precipitates column are only associated to Si and O contamination and not to the Zn-Zr intermetallic phase. Nonetheless, they can be distinguished from Zn-Zr precipitates because of their characteristic shape and smaller size. The smaller bright precipitates in ZK60 samples were studied by TEM (section 4.7), where the surface was prepared by ion milling and is therefore not affected by these contaminations.

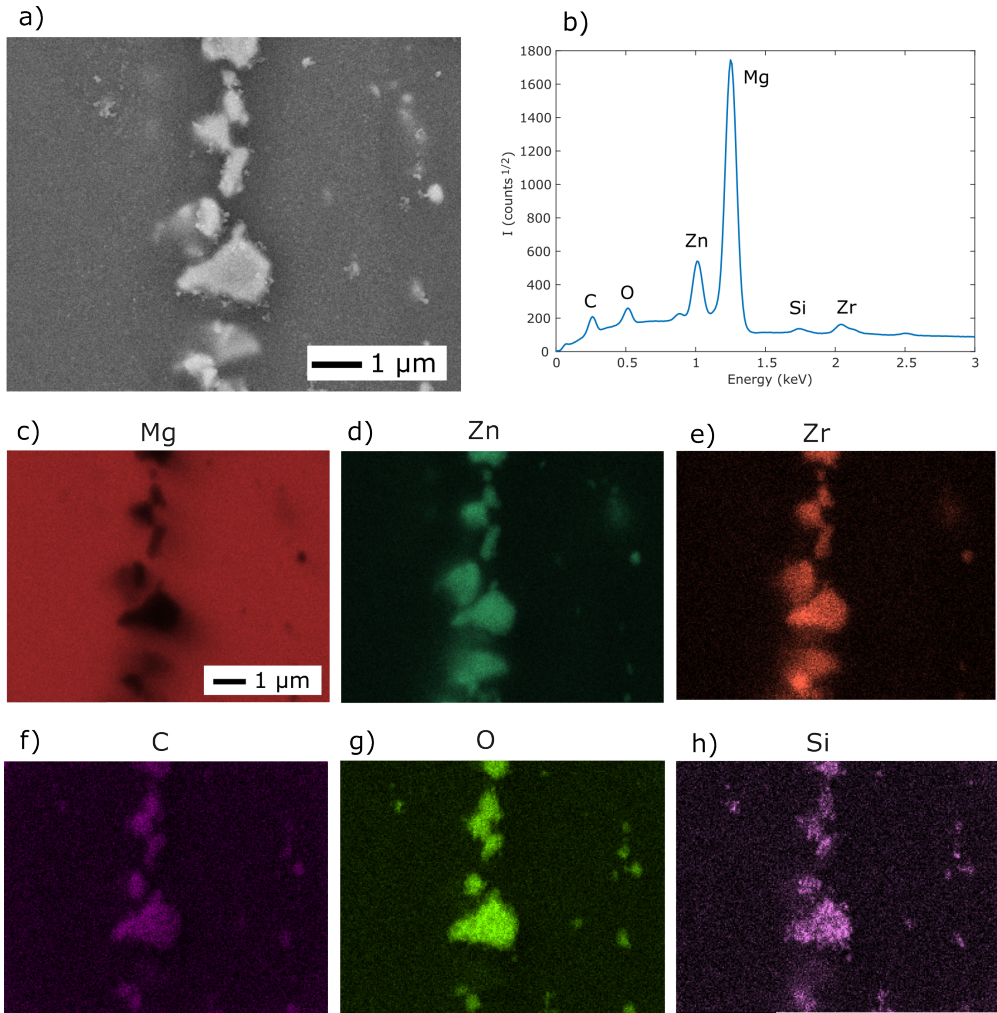


Figure 4.5: EDS maps on the cross section of a undeformed ZK60 sample (see also Figure 4.4). a) image of the analyzed area with InLens detector, b) collected EDS spectrum with peak identification, c) spatial distribution of magnesium, d) spatial distribution of zinc, e) spatial distribution of zirconium, f) spatial distribution of carbon, g) spatial distribution of oxygen, h) spatial distribution of silicon. The observed particles show an increased concentration of Zn and Zr, together with a depletion of Mg. Contamination with C, Si and O is also enhanced close to the precipitates.

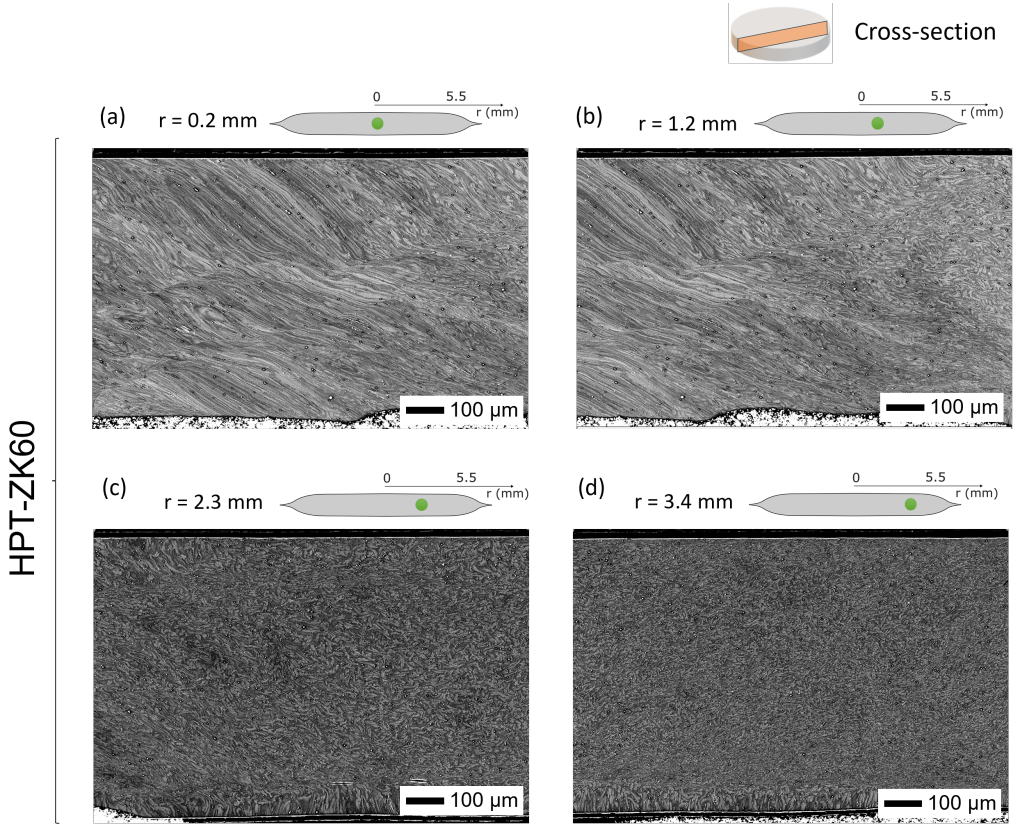


Figure 4.6: SEM micrographs at increasing distance from the disc's center for one HPT-deformed ZK60 sample. The images refer to the sample's cross-section, parallel to the extrusion direction and to the rotation axis for HPT, and are obtained with backscatter electrons contrast. The reported radius refers to the center of the image. The parallel vertical bands observed for undeformed samples are disrupted by HPT. Their resulting length decreases moving towards the edge of the sample.

Figure 4.6 shows SEM images of the cross-section of one HPT-deformed ZK60 sample at different positions varying from its center to its edge. At all positions, the vertical stripes visible for undeformed ZK60 (see Figure 4.4) have been altered by severe plastic deformation. Close to the sample's center (Figure 4.6.a) parallel stripes are still visible although with a more horizontal orientation compared to undeformed samples. Moving towards the edge, the stripes have a more convoluted shape and get progressively thinner and shorter (Figure 4.6.c and 4.6.d). The microstructure at $r = 2.3$ mm and $r = 3.4$ mm is similar to that observed on the sample's surface (see Figure 4.3).

A variation in the microstructure of HPT-samples depending on the distance from the rotation axis is intrinsic to this technique (see section 2.2.1). In fact, the strain responsible for microstructural changes during high pressure torsion depends on the position along the disc's radius. Therefore, the change in shape and size of bright bands can be linked to the applied shear strain, with shorter and thinner bands related to a larger applied shear strain which is located at the larger radius position.

Figure 4.7 shows images of the cross section of HPT-deformed samples at higher magnifications at $r = 0.2$ mm and $r = 2.5$ mm. As can be seen in Figure 4.7.b and 4.7.e, some of the original grain boundaries are visible also after HPT deformation. However, the interior of the grains looks different compared to undeformed sample (see Figure 4.4), showing some BSE electron contrast. A similar contrast is visible also on the sample's surface at similar length scales in Figure 4.3.i and 4.3.l. To have a clearer view of the smaller scale microstructure, a cross-section of HPT-ZK60 was created in the SEM using the Ga-ion FIB at the Zeiss AURIGA SEM at KNMFi. In this way, contamination and possible alterations of the microstructure due to mechanical polishing are avoided; a different contrast was also used, with the InLens SE detector instead of the BSE one. At the highest magnification in Figure 4.8.a, features similar to those previously discussed can be seen. In particular, Figure 4.8.a shows bright particles with a non-uniform distribution and lines similar to the grain boundaries in Figure 4.7, which are indicated by yellow arrows. At higher magnifications (Figure 4.8.c and .d), grains smaller than 100 nm can be observed.

To summarize, ZK60 samples show a complex microstructure both in the as-extruded state and after high-pressure torsion. At lower magnifications, alternating dark and bright bands are observed. The bright band are formed by a high concentration of small particles, appearing bright with BSE contrast. Moreover, chains of larger precipitates in the micrometer range are observed. Using EDS it appears that the larger particles have a high concentration of both alloying elements Zn and Zr. They can therefore be identified with intermetallic phases which are expected in ZK60 samples, such as Zn_2Zr . The smaller particles have been characterized by TEM (see section 4.7), showing a high Zn concentration. These intermetallic phases are not distributed uniformly in the samples. Before HPT, small bright particles have higher concentration in certain areas of the sample, which appear as bright vertical bands, surrounded by areas with a lower density of intermetallic precipitates. Moreover, larger bright particles decorate the grain boundaries of undeformed ZK60.

Intermetallic precipitates are expected in extruded Mg-Zn-Zr alloys as a result of dynamic precipitation during the extrusion process [201–203]. In dynamic precipitation, the diffusion of solute atoms and the nucleation of second-phase precipitates is facilitated by the dislocations formed during the plastic deformation associated to extrusion [203]. These precipitates are regarded to be responsible for the finer grain size of as-extruded ZK60 compared to magnesium, as they stabilize the grain boundaries during the extrusion process [203]. Dynamic precipitation

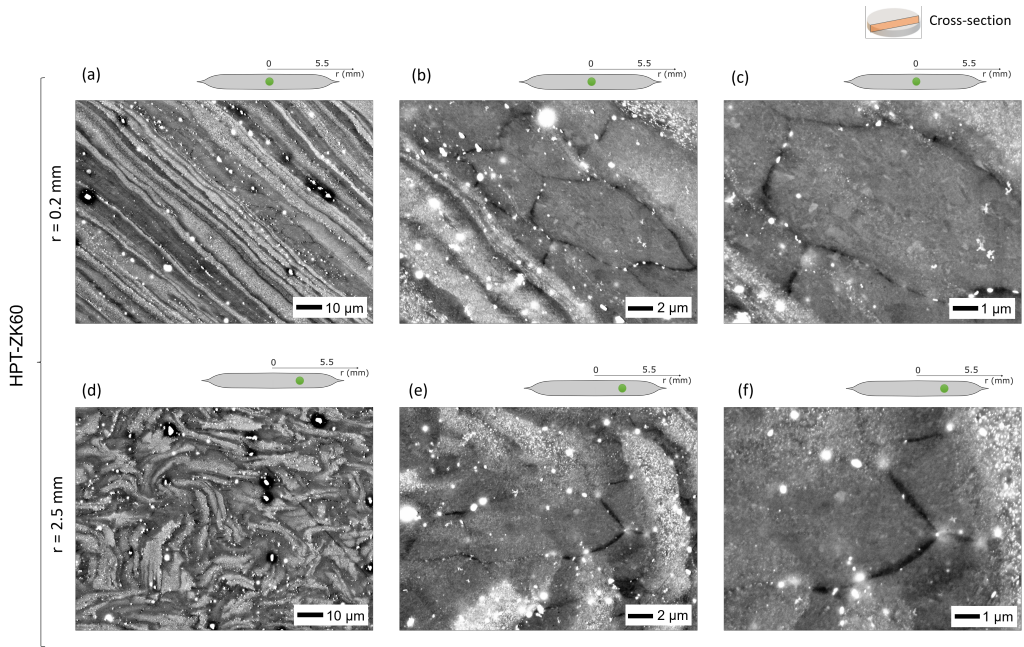


Figure 4.7: SEM micrographs at different length scales for one HPT-deformed ZK60 sample, at a distance of respectively 0.2 mm (a)-(c) and of 2.5 mm (d)-(f) from the disc center. The images refer to the sample's cross-section, parallel to the extrusion direction and to the rotation axis for HPT, and are obtained with backscatter electrons contrast. The reported radius refers to the center of the image. Precipitates bands and grain boundaries of the original grains are visible.

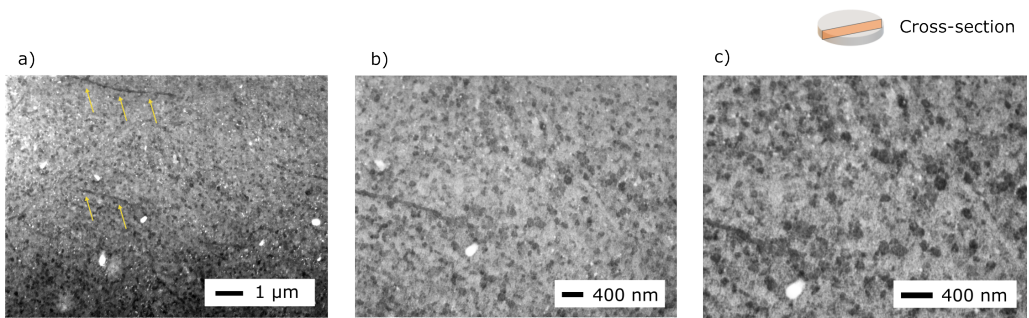


Figure 4.8: SEM micrographs for a HPT-deformed ZK60 sample at different length scales. The images were obtained by creating a cross-section with a Ga-ion FIB and imaging with the InLens detector. Grains smaller than 100 nm can be seen, together with some bright particles and traces of the original grain boundaries (yellow arrows).

is also affected by the extrusion temperature, because at higher temperatures the solubility of Zn and Zr in Mg increases, preventing the precipitation of intermetallic phases. This phenomenon is expected for ZK60 extruded at 573 K according to Ref. [201, 203]. The distribution of intermetallic precipitates in bands may be due to initial chemical inhomogeneities in the cast material, which are stretched during the extrusion process. High pressure torsion alters the shape of the bands containing intermetallic precipitates. After HPT, the bright precipitate bands are no longer parallel to the extrusion direction, and they become shorter and thinner with increasing distance from the rotation axis.

Regarding the grain size, the starting value before HPT is lower than $10\text{ }\mu\text{m}$, which is reduced below 100 nm after severe plastic deformation. Even after high pressure torsion, the original grain boundaries are still visible, suggesting that grain refinement happens within the original ZK60 grains. A similar behavior has been observed in room temperature SPD on Mg-alloys [204, 205]. In general, the fragmentation of original grains in smaller recrystallized grains is typical for continuous dynamic recrystallization in both hexagonal and cubic materials [54, 55].

4.1.3 Grain size distribution before and after HPT-deformation

The effects of HPT on the grain size of magnesium and of ZK60 discs are qualitatively visible from the SEM micrographs presented in the previous sections. Here, these effects are quantified and further discussed.

The grain size analysis as described in section 3.2.1.1 was performed for HPT Mg on the cross-section images at two positions along the radius, using Figure 4.2.b and 4.2.f. The obtained length distribution and the fitted function are shown in Figure 4.9, while the calculated mean value and the variance are given in Table 4.1. As can be seen both in the distribution and from the fit results, no substantial difference is apparent between the sample's center and the mid-radius position regarding the grain size. In both positions, the grain size is strongly reduced by

Table 4.1: Mean value and variance of the grain length distribution resulting from the fits in Figure 4.9 and 4.10.

Sample	Mean length	Variance
as-extruded Mg	$\sim 1\text{ mm}$	-
HPT-Mg ($r \sim 0$)	$0.79\text{ }\mu\text{m}$	$0.22\text{ }\mu\text{m}^2$
HPT-Mg ($r \sim 2.5\text{ mm}$)	$0.79\text{ }\mu\text{m}$	$0.24\text{ }\mu\text{m}^2$
as-extruded ZK60	$7\text{ }\mu\text{m}$	$16\text{ }\mu\text{m}^2$
HPT-ZK60	83.8 nm	0.5 nm^2

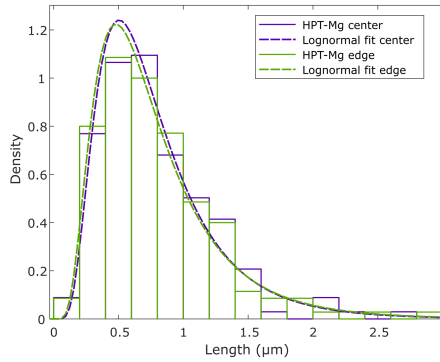


Figure 4.9: Distribution and fitting of the grain length obtained by the line intersection method on the cross section of a HPT-deformed Mg sample (Figure 4.2.b and .f). The distribution was fitted with a lognormal function. No large difference is observed between the center and the edge of the sample.

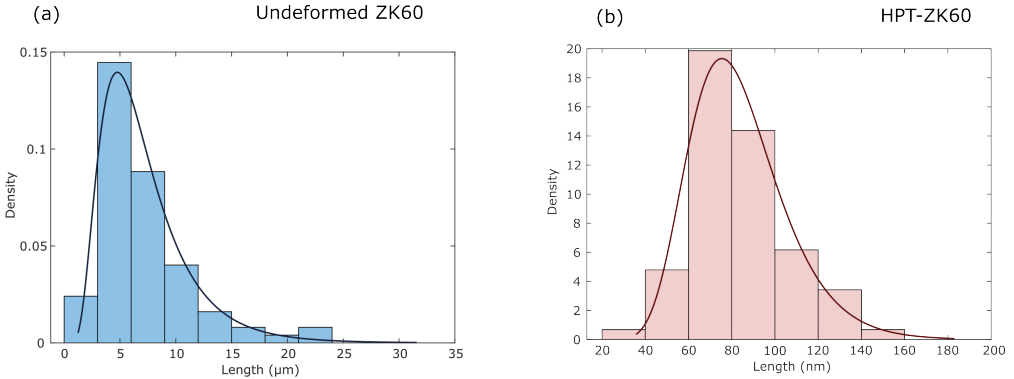


Figure 4.10: Distribution and fitting of the grain length obtained by the line intersection method on the cross section of an Undeformed ZK60 sample (Figure 4.4.d) and a HPT-deformed sample (Figure 4.8.b). The distribution was fitted with a Lognormal function. The grain size distribution moves towards smaller values as an effect of HPT.

HPT – even considering the very large grain size visible in Figure 4.1 for as-extruded samples – reaching values close to $800\ \mu\text{m}$.

For ZK60 samples, the grain size analysis was performed for the undeformed condition using Figure 4.4.d and after HPT deformation using Figure 4.8.b. Since for the HPT-sample not all the grains are clearly visible, it was not possible to perform a convincing line analysis using the same method. Alternatively, the grain dimension was estimated by measuring the length distribution of only the visible grains. This result should therefore be considered only as a rough estimation of the average grain size. The distribution fits are reported in Figure 4.10, while the results are in Table 4.1. In this case, the average grain size before deformation is close to $7\ \mu\text{m}$, although with a large variance of $16\ \mu\text{m}^2$, indicating a wide distribution of grain sizes. After severe plastic

deformation the grain size is greatly reduced, achieving a very small average value of about 84 nm.

4.2 XRD Measurements

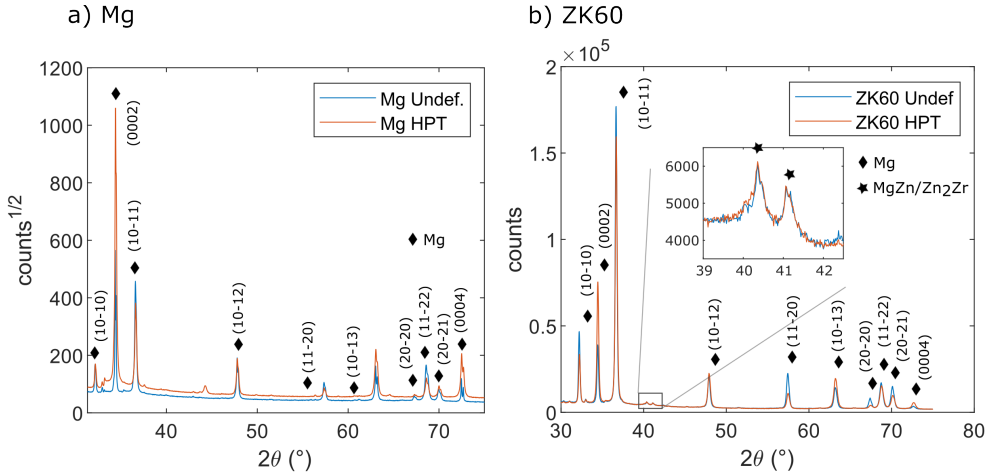


Figure 4.11: a) diffraction pattern for undeformed and HPT-deformed magnesium discs, between 30° and 75°. All the expected peaks for hcp Mg are observed. b) diffraction pattern for undeformed and HPT-deformed ZK60. The expected magnesium peaks are observed together with two extra diffraction peaks between 40° and 42°, which are compatible with MgZn_2

Figure 4.11.a shows the diffraction spectra for Mg discs before and after HPT. All the peaks expected for Mg are identified in the Figure. Figure 4.11.b shows the diffraction spectra for ZK60 before and after HPT. Apart from the Mg diffraction peaks, two smaller peaks are visible at 40.4° and at 41.1°. These peaks have previously been observed in ZK60 and identified with the intermetallic phase MgZn_2 [11, 146, 147, 206, 207].

According to the equilibrium phase diagram reported in Figure 2.2, we may expect the intermetallic phase MgZn in ZK60 at room temperature. However, the metastable phase MgZn_2 is usually reported following extrusion and casting, since these processes happen under non-equilibrium conditions [208].

4.3 Electrochemical H loading of Mg-alloys in 6M KOH

The experimental results of electrochemical loading in 6M KOH are reported in this section. Firstly, the time evolution of the measured surface potential during loading is analyzed for Pd-coated Mg and ZK60 (section 4.3.1). Subsequently, electrochemical isotherms for Pd-coated Mg and ZK60 samples are presented for different deformation states (section 4.3.2) and for different loading parameters (section 4.3.3).

4.3.1 Time evolution of Mg and ZK60 surface potential during electrochemical H loading

The time evolution of the surface potential measured during electrochemical loading of Mg and ZK60 samples, both during the loading step and during the subsequent waiting time (see section 3.4), was monitored for all H loading experiments. As shown in section 3.4.2 for Pd samples, the time evolution of the surface potential after each loading step carries information on eventual hydrogen losses during the waiting time. Therefore, the quality of the experimental results can be evaluated by the stability of the measured potential.

Figure 4.12 shows the surface potential of Mg and ZK60 samples at two different deformation states during stepwise hydrogen loading. The samples were loaded with $j = 80 \mu\text{A}/\text{cm}^2$ for 90 s, followed by a 30 minutes waiting time. Each loading step is represented by one curve: the 90 s loading interval is visible through the increased potential's absolute value, followed by a continuous decrease during the waiting time. A higher density of curves at similar potentials indicates that the surface potential is not changing with increasing hydrogen concentration, which characterizes the $\text{Mg} \rightarrow \text{MgH}_2$ and the $\text{Pd} \rightarrow \text{PdH}_{0.6}$ phase transformations. In fact, as introduced in section 2.3.4, these phase transformations are characterized by a stable chemical potential, leading to a constant measured surface potential. These two zones are visible for all samples, and highlighted in Figure 4.12 by horizontal lines. Between the two zones, the surface potential increases gradually for each subsequent loading step.

The stability of the potential curves can be evaluated by measuring their slope in the last portion of the waiting stage. Figure 4.13 shows an example for a bulk ZK60 sample coated with 100 nm Pd. The curve slope was evaluated with a linear fit in the last 290 s of the waiting period, as highlighted in Figure 4.13.a (gray area). Figure 4.13.b shows the value of the slope as a function of the loading step number.

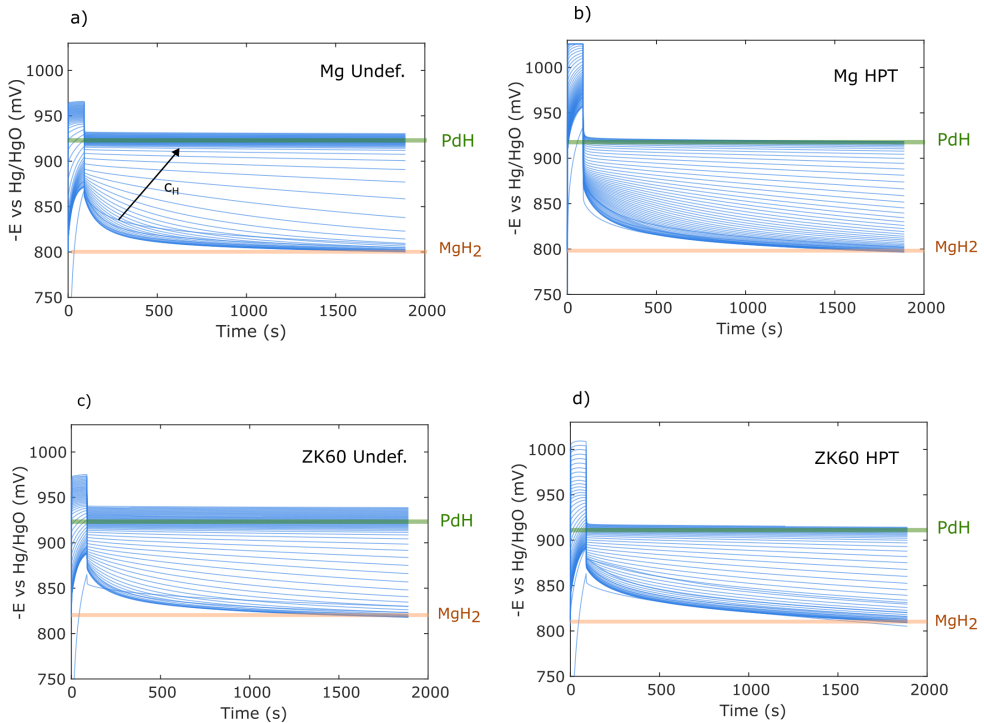


Figure 4.12: Potential curves during electrochemical loading of: a) undeformed Mg, b) HPT-deformed Mg, c) undeformed ZK60, d) HPT-deformed ZK60. The samples were coated with 480 nm Pd, and loaded for 90 s with $j = 80 \mu\text{A}/\text{cm}^2$ at room temperature; after loading no current is applied for 30 min to achieve thermodynamic equilibrium. The equilibrium potentials for MgH_2 and $\text{PdH}_{0.6}$ formation are highlighted by horizontal bands. The potential is highest during the loading steps and then gradually decreases during the waiting interval.

The curves terminating both in the MgH_2 and $\text{PdH}_{0.6}$ equilibrium potentials (for example loading steps 5 and 32, highlighted in Figure 4.13.a) are stable at the end of the waiting time, exhibiting a slope lower than $5 \mu\text{V}/\text{s}$, although the Pd hydride potential appears more stable than the Mg hydride one. The curves terminating in the intermediate region between the two equilibrium potentials exhibit a higher derivative, as can be observed for loading step 16 in Figure 4.13. This determines the peak in the EMF curves slope in Figure 4.13.b.

Achieving a flat potential curve indicates that the allowed waiting time of 30 min is sufficient to reach thermodynamic equilibrium. This condition is fulfilled in the early stages of MgH_2 formation; however, after a certain number of loading steps, the waiting time becomes insufficient for the system to achieve thermodynamic equilibrium, leading to potential curves with a higher derivative. At later stages, the EMF curves only reflect hydride formation in the Pd capping layer. This behavior can be explained by the formation of a MgH_2 blocking layer, and is further discussed in section 5.2.

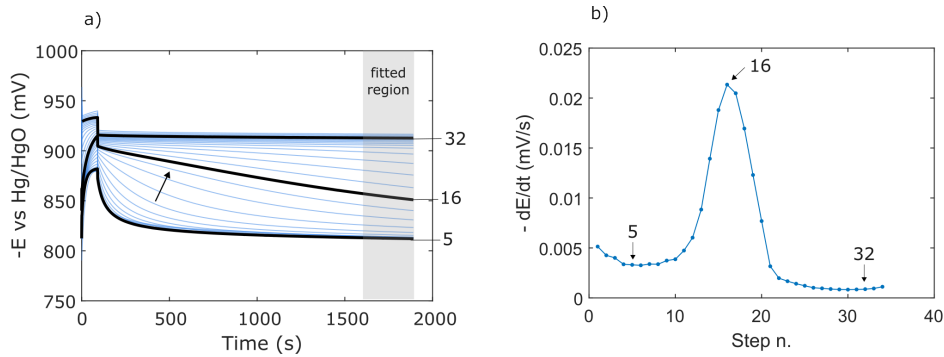


Figure 4.13: a) EMF curves during electrochemical loading of a ZK60 sample coated with 100 nm Pd. Three curves are highlighted in black: loading step 5 (during MgH_2 formation), loading step 31 (during $\text{PdH}_{0.6}$ formation) and loading step 16 (in the transition between the two plateau values). The curves in the transition region have a particular shape, with a shoulder at intermediate potentials pointed by a black arrow. b) derivative of the surface potential as a function of time, obtained with a linear fit to times above 1600 s (gray shaded area in panel a). The derivative is lowest for step 32 (Pd hydride formation), followed by step 5 (Mg hydride formation) and has a maximum in the transition region.

The difference in stability between the surface potential during magnesium and palladium hydride formation can be attributed to properties of the palladium capping layer. At thermodynamic equilibrium (as defined in section 2.4.1), the hydrogen chemical potential is constant in the whole system, including the magnesium and palladium layers. When magnesium hydride has formed, hydrogen exists therefore in the Pd layer as a solid solution, whose concentration adjusts to reach a uniform chemical potential throughout the sample at equilibrium. Experimentally, the surface potential of palladium becomes more stable when increasing H concentration, as can also be seen in Figure 3.4, and achieves the highest stability during Pd hydride formation. The lower stability of the surface potential in the Pd α -phase compared to the hydride phase arises from the greater sensitivity of the potential to small hydrogen losses. Because the experiment measures the surface potential of palladium, these considerations explain why the potential is less stable during magnesium hydride formation – when H is present as a solid solution in Pd – compared to Pd hydride formation.

Finally, we observe that the curves in the intermediate region between Mg and Pd hydride formation, as for example step 16 in Figure 4.12, exhibit a different shape than the typical absorption curves, with a shoulder at potentials between -850 mV and -900 mV, followed by a drop towards lower values. Similar shapes have been observed during preliminary studies on Mg-Pd thin films published by the author and colleagues in Ref. [92], and have been associated to temporary H retention in the Pd layer during the early stages of the Mg hydride blocking layer formation. A similar interpretation is given in literature by Vermeulen et al. [180].

4.3.2 Electrochemical Isotherms of Mg and ZK60 in different deformation states

This section presents the electrochemical isotherms of magnesium and ZK60 samples in different deformation states. Figure 4.14 shows the electrochemical isotherms upon hydrogen loading, measured for Mg and ZK60 samples in the as-extruded and HPT-deformed state. As shown in Figure 4.12, the samples are loaded stepwise with current steps of $80 \mu\text{A}/\text{cm}^2$ for 90 s. The equilibrium potential is measured against a Hg/HgO RE 30 minutes after the end of each loading step. As described in section 3.4, the hydrogen content is given as an equivalent hydride layer thickness t_{MgH_2} (see Eq. 3.1).

The isotherms exhibit two plateaus: the first one, at $\sim -800 \text{ mV}$, is identified with Mg hydride formation while the second one, at $\sim -900 \text{ mV}$, is identified with Pd hydride formation. These potentials are similar to the ones previously reported for Mg-Pd thin films in a similar electrolyte [168, 180], as well as with the results on Pd samples in section 3.4.3. The average value for the equilibrium potential during MgH_2 formation is reported in Table 4.2 for the different isotherms. The equilibrium value is estimated as the average of the potentials in the MgH_2 formation plateau, while the uncertainty is given by: $\Delta E_{eq} = (E_{eq}^{max} - E_{eq}^{min})/2$. In general, Mg-Zn-Zr samples show a slightly higher equilibrium potential compared to pure Mg samples.

The equilibrium potential can be converted to an equivalent hydrogen pressure according to Equation 3.5; the calculated equivalent pressures are also reported in Table 4.2. For Mg hydride

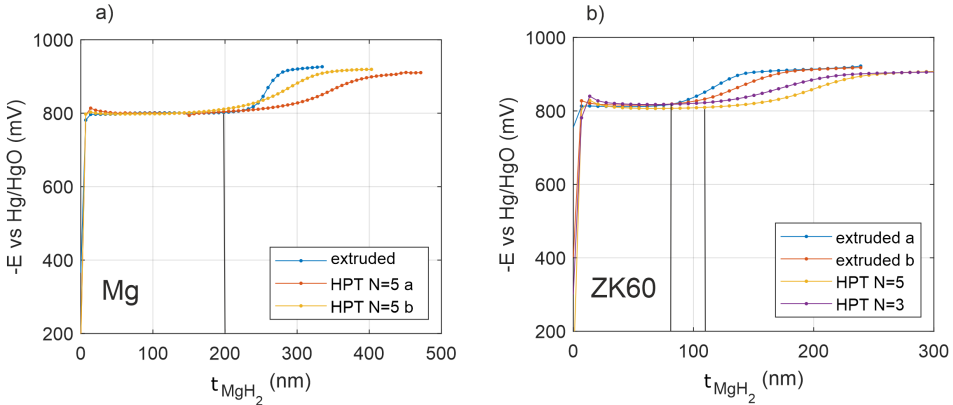


Figure 4.14: Electrochemical isotherms for a) Mg discs as-extruded and after HPT deformation and b) ZK60 discs as-extruded and after HPT deformation. For pure Mg, HPT does not affect the width of the potential plateau for MgH_2 formation, while for ZK60 the plateau width increases after HPT.

Table 4.2: Equilibrium potential and equivalent H pressure for the isotherms in Figure 4.14. The equivalent hydrogen pressure is calculated according to Equation 3.5.

Sample	Condition	$-E_{eq}$ (mV)	p_{H_2} (μ bar)
Mg	As-extruded	799 ± 3	3.93 ± 0.01
	HPT(5 GPa, N=5, 1rpm) a	801 ± 7	4.74 ± 0.03
	HPT(5 GPa, N=5, 1rpm)	799 ± 2	3.90 ± 0.01
ZK60	As-extruded a	812.4 ± 0.9	11.12 ± 0.01
	As-extruded b	818 ± 6	17.7 ± 0.1
	HPT (5 GPa, N=5, 1rpm)	810 ± 10	10.3 ± 0.1
	HPT (5 GPa, N=3, 1rpm)	820 ± 10	23.2 ± 0.2

formation the value is around 4μ bar, while for ZK60 it is between 10μ bar and 20μ bar. ZK60 pressure-concentration isotherms in the 473 K - 623 K range also report plateau pressures close to those of pure Mg [9, 149]. These equilibrium pressure for hydride formation were used to select the appropriate starting pressure for the gas loading experiments, which was set to 0.1 mbar to provide a sufficient overpotential as described in section 3.5.

The obtained equilibrium pressures are contextualized in the van't Hoff plot in Figure 4.15, which gives the equilibrium pressure for hydride formation and decomposition as a function of temperature for Mg bulk and thin film samples. The equilibrium pressure for the $MgH_2 \rightarrow Mg$ phase transformation at 300 K, is $p_{H_2}^{eq} \simeq 1.2 \mu$ bar according to the van't Hoff equation (see section 2.3.4), using $\Delta H = -74.5 \text{ kJ/mol}$ and $\Delta S = -135 \text{ J/mol}$ [94]. This value cannot be directly compared to the equilibrium pressure for hydride formation, because of the known hysteresis effect leading to higher pressures for hydride formation than for its decomposition; moreover, we should consider that the enthalpy and entropy of formation in Ref. [94] were measured at temperatures between 600 and 850 K. As expected, the measured equilibrium potentials for hydride formation are higher than the theoretical values for hydride decomposition but in the same order of magnitude. These results, together with the good match of the equivalent pressure for palladium hydride formation in section 3.4.3, validate the conversion from equilibrium potential to equilibrium pressure according to Equation 3.5.

The relation between the hydride formation equilibrium pressures in Mg and ZK60 is now further discussed. Two references are reported in the van't Hoff plot in Figure 4.15 regarding hydride formation and decomposition in ZK60. In the work of Krystian et al. [9], the equilibrium pressures for hydride formation in ZK60 is lower compared to Mg at similar temperatures. However, the complete isotherms were not evaluated in this reference due to the slow absorption kinetics, and so the reported value corresponds to the pressure on the left side of the two-phase region.

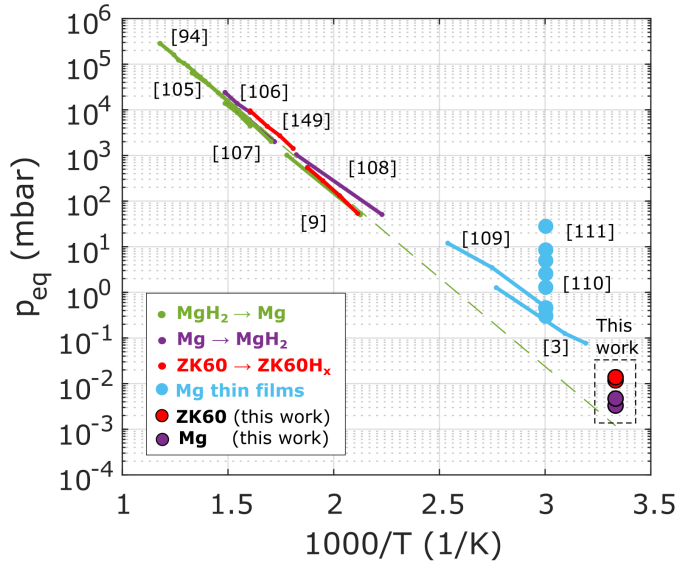


Figure 4.15: Van't Hoff plot based on literature data during hydride formation (purple) and decomposition (green) for bulk Mg [94, 105–108]. Data related to Mg thin films is also reported in light blue [3, 109–111]. Data related to hydride formation in ZK60 is shown in red [9, 149]. The green dashed line gives the equilibrium pressure as a function of temperature according to Eq. 2.7, considering $\Delta H = -74.5 \text{ kJ/mol}$ and $\Delta S = -135 \text{ J/(molK)}$ [94]. The red points represent the equilibrium pressure for hydride formation in ZK60, while the blue points represent the results for Mg thin films on different substrates. The equivalent equilibrium pressures at room temperature in Table 4.2 are plotted on the right hand side and show a good agreement with the literature.

Therefore, it is possible that the equilibrium pressure for hydride formation in ZK60 was underestimated. The work of Skrypnuk et al. [149] refers to ZK60 processed by ECAP and High Energy Ball Milling (HEBM). No hysteresis was observed between loading and unloading equilibrium pressures for ZK60 processed by ECAP+HEBM. This is explained by the reduced particle size of the powder obtained by HEBM, which is close to 25 nm and therefore in a similar range to the critical size of a MgH_2 nucleus. This would reduce the stress between the hydride nucleus and the metal matrix, which is responsible for the hysteresis (see section 2.3.4). The equilibrium pressure for hydride decomposition reported by Skripnyuk et al. [149] for ZK60 is higher than for Mg in a similar temperature range. In cases where hysteresis is not suppressed, we can then expect the equilibrium pressure for hydride formation in ZK60 to also be higher than in Mg. This is in fact observed in this work for hydride formation in bulk samples at room temperature, where no suppression of the hysteresis is expected and ZK60 shows a slightly higher equilibrium pressure compared to magnesium (see Figure 4.15).

Considering the effects of high-pressure torsion on hydride phase formation, no clear difference is found for Mg samples (Figure 4.14.a), where extruded and HPT-deformed samples show a

similar plateau width and an equivalent thickness of the hydride layer of $\simeq 200$ nm. For ZK60 samples (Figure 4.14.b), the measured equivalent hydride thickness is almost half of that observed in pure magnesium. However, ZK60 shows a difference between as-extruded discs, where $t_{\text{MgH}_2} \simeq 80$ nm, and HPT-deformed discs, where the equivalent hydride thickness increases to $t_{\text{MgH}_2} \simeq 110$ nm. These effects are further discussed in section 5.2, taking into account the microstructure of the samples and the results of FEM simulations.

4.3.3 Loading current effects on Mg and ZK60 isotherms

In this last section related to electrochemical loading results, the effects of different loading current densities on Mg and ZK60 electrochemical isotherms are presented. As introduced in section 2.3.5, the applied current density and the duration of the current pulse determine the driving force to hydride nucleation, therefore modifying the kinetics of hydride formation (see Eq. 2.25 and Eq. 2.8). The effect of the loading current density on hydride formation was investigated by loading Mg and ZK60 samples with different current densities. In particular, a current density of either $j = 20 \mu\text{A}/\text{cm}^2$ or $j = 80 \mu\text{A}/\text{cm}^2$ was applied for 90 s. The electrochemical isotherms were then constructed as in the previous section, by taking the equilibrium potential vs Hg/HgO after 30 min.

Figure 4.16 shows the results for Mg and ZK60 samples. For both materials, the samples loaded with a lower current density show a larger hydride layer thickness than those loaded with a higher current density. In particular, the hydride layer thickness grows from ~ 200 nm in to ~ 480 nm in Mg and from ~ 80 nm to ~ 240 nm in ZK60. This phenomenon can be attributed to the effect

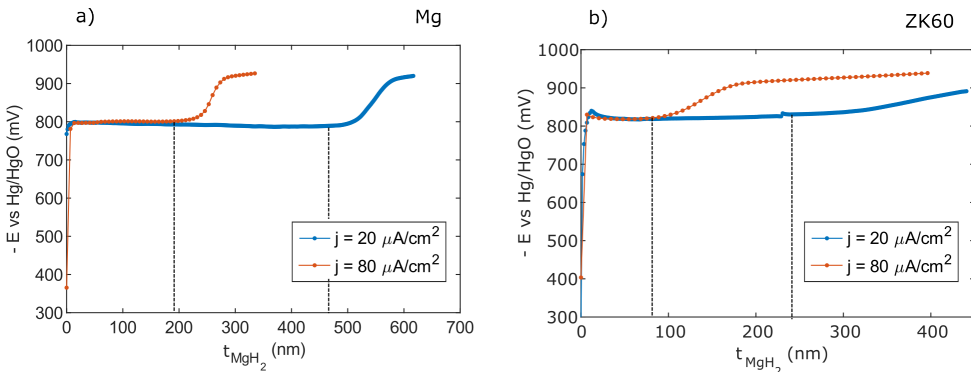


Figure 4.16: Electrochemical isotherms for a) bulk Mg coated with 100 nm Pd and b) bulk ZK60 samples coated with 500 nm Pd, loaded with different current densities of $j = 20 \mu\text{A}/\text{cm}^2$ (in blue) and $j = 80 \mu\text{A}/\text{cm}^2$ (in orange) for 90 s. For both materials, the hydride layer thickness is larger when using a lower loading current density.

of the driving force to hydride nucleation on the achieved blocking layer thickness, as will be further discussed in section 5.2.

These curves allow for two other important considerations. Firstly, thanks to the higher resolution obtained through the lower loading current density we can estimate the solubility limit for H in α -phase Mg at room temperature, which is determined to be $(2.6 \pm 0.2) \times 10^{-5}$ H/Mg for bulk Mg and $(2.3 \pm 0.2) \times 10^{-5}$ H/Mg for ZK60 (see Figure 4.16). The error on the solubility limit is estimated as half of the concentration step introduced during loading. Since the two values overlap within their error bars, it appears that the different chemical composition does not measurably affect the hydrogen solubility in α -phase Mg.

Secondly, the effect of the Pd hydride layer thickness on the isotherm slope in the transition zone between the two plateau regions becomes apparent in Figure 4.16, where the Mg samples were coated with 100 nm Pd, while the ZK60 samples were coated with 500 nm Pd. The transition between the Mg hydride and Pd hydride plateaus is sharper for the samples with a thinner Pd coating, because the same loading step introduces a larger concentration change in the thinner Pd layer, which is associated to a larger change in the measured surface potential. The hydrogen concentration is assigned in these isotherms only to the magnesium volume (see Eq. 3.1 for determining the equivalent hydride layer thickness). By calculating the actual concentration in the palladium capping layer, all the curves would have the same slope in the transition zone between the magnesium hydride and the palladium hydride plateaus. Since the process of interest in this work is magnesium hydride formation, however, it would not make sense to alter the concentration measure to include the palladium capping layer. For the same reasons explained so far, variations in the thickness of the Pd coating layer explain the different slopes in the transition zone between the magnesium and the palladium hydride plateaus of the isotherms in Figure 4.14. The thickness of the Pd capping layer does not affect the potential during magnesium hydride formation because, regardless of the layer thickness, the same potential value will be reached at thermodynamic equilibrium with the magnesium hydride phase.

4.4 FEM Simulations of Grain Boundary Diffusion in MgH₂

FEM diffusion simulations were performed according to section 3.6 to understand the role of hydrogen diffusion along grain boundaries during room temperature electrochemical H loading, after the formation of a magnesium hydride blocking layer. Hydrogen transport in MgH₂ and at grain boundaries was investigated for samples of different microstructure. The simulation focuses on hydrogen content in the palladium capping layer, which in turn affects the surface potential measured during electrochemical H loading.

Before the formation of the blocking layer, hydrogen can diffuse in α -Mg with a coefficient of $D_H \sim 10^{-11} \text{ m}^2/\text{s}$ at room temperature (see section 2.3.6) and the waiting time of 30 min between loading steps is sufficient to reach thermodynamic equilibrium, as the experimental results in section 4.3.1 confirm. After the blocking layer is formed, diffusion becomes much slower: according to the literature discussed in section 2.3.6, we expect a diffusion coefficient as low as $D_H \sim 10^{-28} \text{ m}^2/\text{s}$ in MgH_2 grains, and a faster diffusion coefficient at grain boundaries. For this simulation, the highest reported value of $D_H \sim 10^{-16} \text{ m}^2/\text{s}$ [114] is chosen for grain boundaries diffusion.

The main question addressed by the FEM simulation is whether the waiting time of 30 min between electrochemical loading steps is sufficient to observe effects of grain boundary diffusion, depending on the average grain size of the sample. To address this question, the model illustrated in section 3.6.1 was used, always consisting in a 350 nm MgH_2 layer with grain boundaries, capped by 500 nm palladium. The total MgH_2/Mg layer thickness is 850 nm. As introduced in section 3.6.1, the grain boundaries are simulated only in magnesium hydride to optimize the meshing and computation time and the simulated area was scaled with the grain size to include the same number of grain boundaries in the domain. As described in the previous section, during electrochemical loading hydrogen is introduced from the sample's surface into the palladium layer. To reach thermodynamic equilibrium, hydrogen must diffuse through the magnesium hydride blocking layer in order to reach the underlying α -Mg volume, which is then transformed to MgH_2 . The diffusion continues, and the hydrogen concentration in the palladium layer decreases, until the chemical potential of hydrogen in palladium is equal to that of hydrogen in magnesium hydride. The expected H concentration in palladium for the chemical potential corresponding to MgH_2 formation is known from electrochemical isotherms, and corresponds to about 0.009 H/Pd (see also Figure 4.18). With this information and the FEM simulation we can therefore estimate the characteristic time necessary to reach thermodynamic equilibrium and compare it to the experimental wait time during electrochemical loading.

Figure 4.17 shows the results of the FEM simulations for the different considered grain sizes during the second simulation step. As described in section 3.6.1, in the first simulation step a hydrogen flux is actively introduced in the Pd capping layer for 90 s, while in the second step hydrogen is let to diffuse from the Pd layer through the MgH_2 layer without imposing an external flux. The achieved local hydrogen concentration is plotted as a function of the lateral position at 50 nm intervals. The different curves represent the H distribution every 30 minutes, for a total of 30 hours. For all grain sizes, the concentration after 90 s of loading at $8.25 \times 10^{-6} \text{ mol}/(\text{m}^2\text{s})$ — corresponding to a current of $80 \mu\text{A}/\text{cm}^2$ during electrochemical loading — is close to 0.022 H/Pd in the Pd layer and close to zero in the MgH_2 and Mg layers. The time evolution then depends on the hydrogen flux through the blocking layer and, thus, on the chosen grain size. For grains of $d = 100 \text{ nm}$ (Figure 4.17.a), hydrogen concentration in the Pd layer

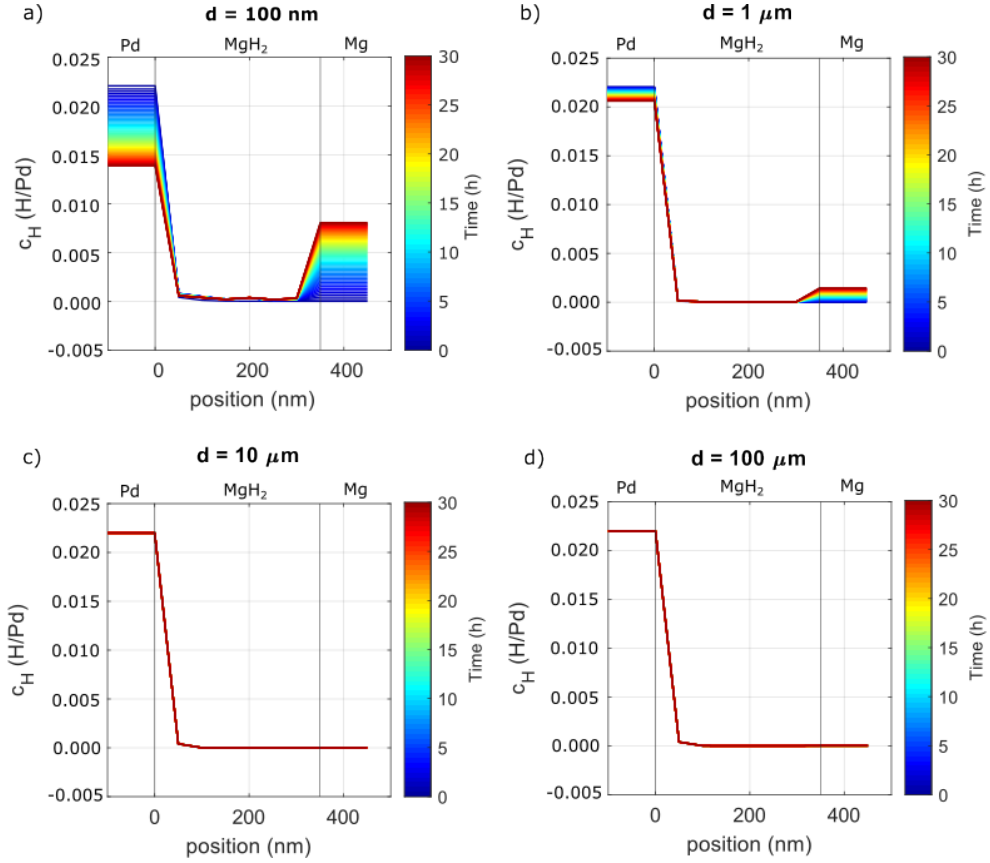


Figure 4.17: H concentration distribution in FEM diffusion simulation for grain sizes of: a) 100 nm, b) 1 μm , c) 10 μm and d) 100 μm . The plotted concentration is calculated by line averaging every 50 nm and normalised to H/Pd. The H distribution is evaluated and plotted every 30 minutes for 30 hours. Only for the two lower grain dimensions (panels a and b) a significant change of the H content in the Pd capping layer is observed as a function of time. The total thickness of the MgH_2/Mg layer is 850 nm, of which only the first 450 nm are represented in the diagrams.

decreases gradually, reaching a final value close to 0.014 H/Pd after 30 hours. In the meantime, H concentration in the Mg layer gradually increases. In a real experiment, hydrogen diffusing past the hydride blocking layer and reaching the $\alpha\text{-Mg}$ area would transform in MgH_2 instead of accumulating in Mg. Since the focus of this simulation is the hydrogen content in the Pd layer, which controls the measured surface potential during electrochemical loading, this aspect can be disregarded. In this case, H accumulation in the $\alpha\text{-Mg}$ layer simply indicates a relevant diffusion through the hydride layer. The resulting concentration are constant in Mg because of the long diffusion times, which allow to reach a uniform H distribution. For the smallest grain size of 100 nm, the transported hydrogen would increase the hydride layer thickness by 2.15 nm after 30 h of diffusion.

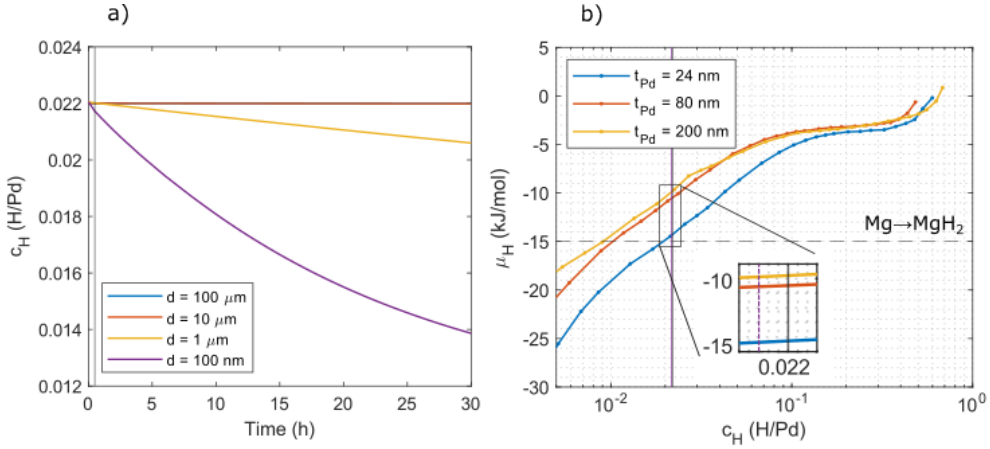


Figure 4.18: a) Hydrogen concentration in the Pd layer as a function of time for the different grain sizes. The vertical line marks 30 minutes after the start of the second simulation step. b) isotherms of Pd thin films from Wagner et al. [21]. The concentrations achieved after 30 minutes of diffusion according to panel a) are marked on the isotherm; the black vertical line marks the H-concentration in Pd at $t = 0$ min, right after the end of the loading step, while the dotted violet line indicates the concentration in palladium at $t = 30$ min for a grain size of $d = 100 \text{ nm}$. The horizontal dashed line marks the equilibrium chemical potential for the $Mg \rightarrow MgH_2$ phase transformation, corresponding to a concentration of 0.009 H/Pd, which is the initial condition of the simulation and represents thermodynamic equilibrium between H in palladium and in magnesium hydride. The waiting time of 30 min is not sufficient to return to the initial H concentration in Pd, indicating that thermodynamic equilibrium via grain boundary diffusion in magnesium hydride cannot be reached in this time interval.

Figure 4.18.a shows the resulting H concentration in the Pd layer as a function of time. The concentration drop in the Pd layer after 30 minutes is pointed by a vertical line. This time interval corresponds to the waiting time after each loading step in electrochemical loading. The lowest concentration in palladium after 30 min of diffusion is observed for the 100 nm average grain size, and corresponds to 0.0217 H/Pd. The equilibrium chemical potential for MgH_2 formation can be calculated from the equilibrium potential of -800 mV vs Hg/HgO measured in section 4.3.2. According to $\mu_H = -F(E(Hg/HgO) + E_f(Hg/HgO))$ we obtain $\mu_H = -15.4 \text{ kJ/mol}$ (using E_f as defined in section 3.4.1). From the Pd electrochemical isotherms in Figure 4.18.b, we can see that we would need a hydrogen concentration close to 0.009 H/Pd in the Pd capping layer to match the MgH_2 chemical potential at thermodynamic equilibrium. Therefore, with the chosen waiting time, it is not possible to achieve thermodynamic equilibrium by the diffusion of hydrogen through a 350 nm thick magnesium hydride blocking layer, even considering the effect of grain boundaries. It should be noted that a waiting time of 30 h would still not be sufficient to reach thermodynamic equilibrium, given a grain size of 100 nm.

Nonetheless, we can estimate how the small concentration variation in the capping layer due to grain boundary diffusion affects the Pd surface potential after 30 min. In fact, during electrochemical loading the surface potential of Pd is measured as a function of time, and the value after

30 min is plotted as a function of hydrogen concentration to create electrochemical isotherms. The objective now is to evaluate whether, despite not reaching thermodynamic equilibrium, diffusion through grain boundaries might still affect the measured isotherms. The biggest drop of 3×10^{-4} H/Pd is observed for the smaller grain size of 100 nm. To estimate the potential drop related to this concentration change, the Pd-H thin film isotherms from Wagner et al. [21] in Figure 4.18.b can be used. There, the equilibrium chemical potentials are plotted for films of varying thicknesses as a function of the hydrogen concentration. In the alpha-phase region, the chemical potential steadily increases with the logarithm of hydrogen concentration. Even though the absolute chemical potential values are different, the measured slopes of $\mu_H(\log(c_H))$ are similar for 24 – 200 nm Pd film thickness. Hence, a measured potential variation can be correlated with the corresponding drop in concentration. Reading from the graph, a chemical potential drop of 0.159 kJ/mol is related to a concentration drop of 3×10^{-4} H/Pd; this corresponds to a 1.64 mV variation in the surface potential, considering that $\Delta\mu_H = \Delta E/F$. In the present work, this drop results from H diffusion from the palladium layer to the Mg hydride layer after 30 minutes, considering a grain size of 100 nm and a hydrogen diffusion coefficient of 10^{-16} m²/s at grain boundaries and of 10^{-28} m²/s in MgH₂ grains.

The –1.64 mV potential change due to diffusion can be compared to the change caused by hydrogen accumulation in the Pd layer after the loading step. The initial condition of the simulation corresponds to 0.009 H/Pd (see Table 3.4), which would give a potential in equilibrium with that of MgH₂ formation, indicated by the horizontal dashed line in Figure 4.18.b. After loading for 90 s, the concentration increases to 0.022 H/Pd, which would lead to a potential increase of 30 mV according to the isotherm in Figure 4.18.b. After 30 minutes of diffusion through grain boundaries, the potential would then drop by –1.64 mV. The drop caused by diffusion is therefore small compared to the 30 mV increase expected from H accumulation in the Pd layer. How this simulation result relates to the experimental results for electrochemical and gas-phase loading will be further discussed in section 5.2.

4.5 Gas Volumetry

As observed in sections 4.3 and 4.4, electrochemical loading is not suitable to observe effects related to hydrogen diffusion at grain boundaries because of the limited diffusion time allowed between loading steps, and because only the surface potential of the Pd coating can be measured. Therefore, a complementary experimental technique allowing for extended diffusion times is necessary to measure differences related to hydrogen diffusion at GBs. In this work this is achieved by gas-phase hydrogen loading. Mg and ZK60 samples in different deformation states were hydrogenated at room temperature and at 398.2 K according to section 3.5. The results of those experiments are reported respectively in section 4.5.1 and 4.5.2.

4.5.1 Room Temperature Hydrogen loading

Hydrogen absorption was studied at room temperature for Mg and ZK60 sample in the as-extruded and HPT-deformed states according to section 3.5. These measurements allow to observe differences in the absorption kinetics and in the overall amount of absorbed hydrogen (hydrogen capacity) as a function of the samples' microstructure and chemical composition. Differently to electrochemical loading, this experimental technique allows for very long absorption times.

Figure 4.19 shows the hydrogen gas absorption isotherms of as-extruded and HPT-deformed Mg samples. The samples were loaded in up to 9 steps with a starting pressure of $P_0 = 0.1$ mbar, each until a stable pressure was achieved, indicating that hydrogen was no longer being absorbed in the sample. Afterwards, the chamber was again filled to 0.1 mbar, restarting the absorption process. The experiment was stopped when, after refilling the chamber to 0.1 mbar, no pressure drop could be observed, as visible in step 6 for Mg (see Figure 4.19.a) and in step 10 for HPT-Mg (see Figure 4.19.b). Since no unloading was performed between the steps in Figure 4.19, the total amount of absorbed hydrogen is given by the sum of the values calculated for each single step.

The loading temperature and absorbed moles of hydrogen n_H according to Eq. 3.7 are reported in Table 4.3. In the first loading steps for undeformed Mg, a stable pressure value is reached within 10 hours. The absorption becomes slower in the second-to-last and last loading steps. For HPT-Mg, absorption is overall slower, however more curves could be measured before absorption stopped. This aspect is further discussed in section 5.3.

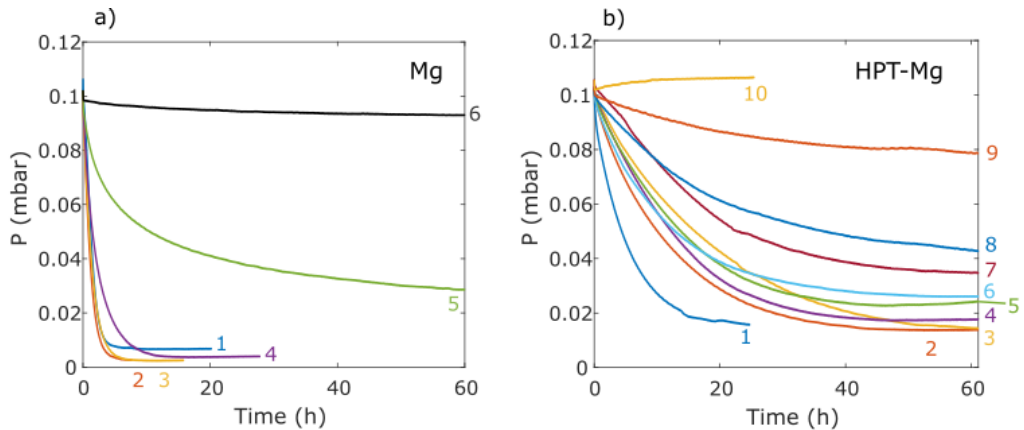


Figure 4.19: Hydrogen absorption curves for a) as-extruded Mg and b) HPT-deformed Mg. For HPT-Mg more loading steps could be performed before hydrogen absorption stopped.

Table 4.3: Temperature, amount of absorbed hydrogen, equivalent hydride layer thickness and fitted JMAK exponent for the loading steps of Mg and ZK60 in as-extruded state and after HPT.

Sample	Step n.	Temperature (K)	n_H (10^{-7} mol)	Eq. t_{MgH_2} (nm)	JMAK exponent
Mg	1	295.8 ± 0.3	6.85 ± 0.04	79.2 ± 0.9	1.321 ± 0.001
	2	295.8 ± 0.4	7.08 ± 0.04	161 ± 1	0.9335 ± 0.0008
	3	296.0 ± 0.3	7.05 ± 0.04	243 ± 2	0.9019 ± 0.0009
	4	294.8 ± 0.9	6.97 ± 0.04	323 ± 2	0.8542 ± 0.0006
	5	295.5 ± 0.9	5.21 ± 0.03	383 ± 2	0.6731 ± 0.0007
	6	296.0 ± 0.6	0.48 ± 0.06	389 ± 2	-
HPT-Mg	1	292 ± 3	6.25 ± 0.05	59.7 ± 0.9	0.700 ± 0.002
	2	292 ± 1	6.43 ± 0.04	121.1 ± 0.9	0.8928 ± 0.0009
	3	292 ± 3	7.58 ± 0.06	194 ± 1	0.9930 ± 0.0002
	4	295 ± 1	6.06 ± 0.04	251 ± 1	0.9436 ± 0.0004
	5	298 ± 2	5.63 ± 0.04	305 ± 1	0.8514 ± 0.0003
	6	290 ± 4	5.54 ± 0.05	358 ± 1	0.7588 ± 0.0002
	7	293 ± 2	4.89 ± 0.03	405 ± 1	-
	8	294 ± 2	4.57 ± 0.03	449 ± 1	0.8465 ± 0.0003
	9	294 ± 2	1.73 ± 0.01	465 ± 1	0.857 ± 0.001
ZK60	1	295.2 ± 0.7	6.04 ± 0.03	69.6 ± 0.4	0.973 ± 0.004
	2	295.4 ± 0.5	6.43 ± 0.04	142.2 ± 0.6	0.885 ± 0.001
	3	295.3 ± 0.7	5.46 ± 0.03	205.1 ± 0.7	0.798 ± 0.001
	4	295.4 ± 0.7	4.29 ± 0.02	254.6 ± 0.7	0.7787 ± 0.0007
	5	296 ± 2	2.75 ± 0.02	285.7 ± 0.8	-
HPT-ZK60	1	294 ± 1	4.76 ± 0.03	44.9 ± 0.6	-
	2	294 ± 2	4.76 ± 0.03	90.3 ± 0.8	1.070 ± 0.006
	3	293 ± 3	4.15 ± 0.03	130 ± 1	1.119 ± 0.003
	4	294 ± 2	4.14 ± 0.03	169 ± 1	1.202 ± 0.003
	5	293 ± 3	4.01 ± 0.03	208 ± 1	-
	6	295 ± 2	3.84 ± 0.03	244 ± 1	1.343 ± 0.001
	7	294 ± 3	4.23 ± 0.03	285 ± 1	-
	8	294 ± 2	3.60 ± 0.02	319 ± 2	1.302 ± 0.001
	9	293 ± 1	3.40 ± 0.02	351 ± 1	1.513 ± 0.004
	10	294 ± 2	3.14 ± 0.02	380 ± 2	-
	11	294 ± 1	2.86 ± 0.02	407 ± 2	1.342 ± 0.003
	12	294 ± 2	2.23 ± 0.01	428 ± 2	1.649 ± 0.002
	13	294 ± 1	2.43 ± 0.02	451 ± 2	1.86 ± 0.01
	14	294 ± 2	2.09 ± 0.01	471 ± 2	-

Overall, the HPT-deformed sample absorbs a larger amount of hydrogen. However, due to HPT deformation this compressed sample with a diameter of 11 mm also has a larger surface area compared to as-extruded Mg, which has a diameter of 10 mm. To exclude an effect only caused by the different surface-to-volume ratio, an equivalent hydride layer thickness t_{MgH_2} was calculated according to Equation 3.1, using the total surface area of the sample. The achieved equivalent layer thickness after each loading step is also reported in Table 4.3. After surface normalization, the equivalent layer thickness is larger in HPT-Mg, reaching (465 ± 1) nm as opposed to the (389 ± 2) nm of undeformed Mg. This indicates that the larger amount of hydrogen absorbed in HPT-samples is not only an effect of the sample geometry.

A JMAK analysis was performed as described in section 3.5.3 to gain information on magnesium hydride the nucleation and growth modes.

Figure 4.20 shows the JMAK analysis curves, while the fitted JMAK exponents are reported in Table 4.3. For Mg, an initial value of 1.3 is observed, followed by decreasing exponents between 0.93 and 0.67. This behavior is similar to what is observed at higher temperatures during hydride formation, where JMAK exponents between 0.6 and 1.6 are reported for loading at 663 K [209]. A JMAK exponent close to 1 can be interpreted as the nearly 2D diffusion-limited growth or the nearly 1D interface-limited growth of a fixed number of hydride nuclei. Alternatively, it may also represent a linear increase of the number of hydride nuclei without growth (see section 3.5.3).

For HPT-Mg the JMAK curves are less linear and therefore cannot be entirely fitted with a straight line. This indicates that a nucleation and growth mechanism is overall less suitable to describe hydride formation in this case. The obtained exponents are still changing between 0.7

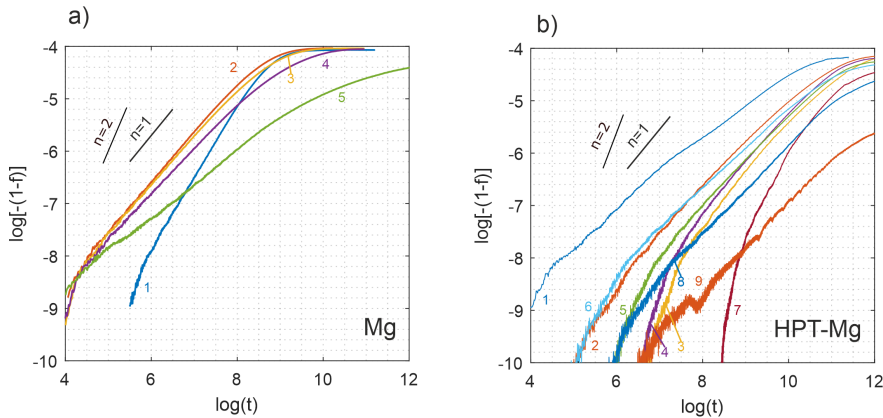


Figure 4.20: JMAK analysis for a) as-extruded Mg discs for loading 1 to 5 and b) HPT-Mg discs for loading 1 to 9. Lines with a slope of $n = 1$ and $n = 2$ are added as a guide; the fitted exponents are reported in Table 4.3.

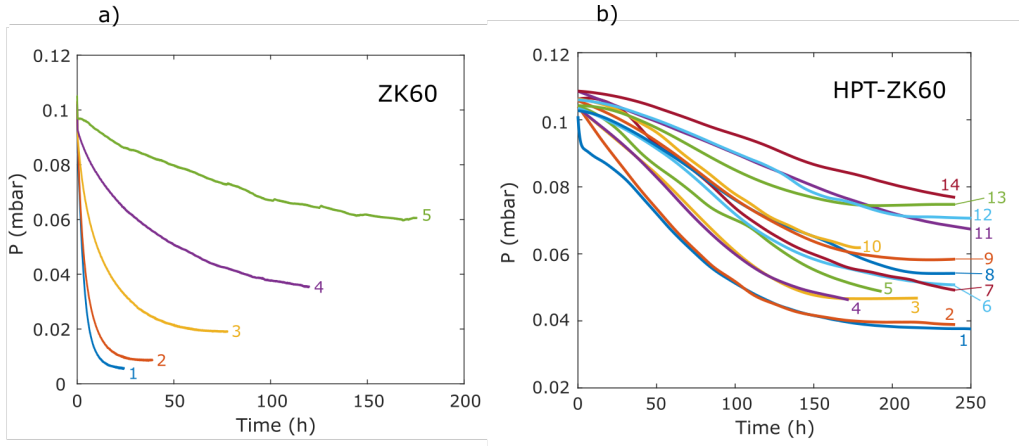


Figure 4.21: Hydrogen absorption curves for a) as-extruded ZK60 and b) HPT-deformed ZK60. For HPT-ZK60 more loading steps could be performed before hydrogen absorption stopped.

and 0.99, in a similar range to those observed for undeformed Mg. This will be further discussed in section 5.3.

Figure 4.21 shows the absorption isotherms for ZK60 samples as-extruded and after HPT deformation. For each loading step, the temperature, moles of absorbed hydrogen n_H and equivalent hydride thickness t_{MgH_2} are reported in Table 4.3. The different diameter of as-extruded and HPT discs is taken into account in calculating the equivalent hydride layer thickness. In the as-extruded state (Figure 4.21.a), the samples can be loaded 5 times consecutively, until no more hydrogen is absorbed. On the contrary, with HPT hydrogen absorption stops after 14 loading steps (Figure 4.21.b). Interestingly, the absorption kinetics is generally faster for undeformed ZK60, although the time necessary to reach equilibrium strongly increases for each subsequent loading step. The absorption curves for HPT-ZK60 all show similar absorption times, which are longer than those of undeformed samples, except for the first loading curve. During the first absorption, a first fast pressure drop is followed by a small plateau and by a second decrease in pressure afterwards. Similar behavior has previously been observed by Cengeri et al. for ZK60 samples at higher temperatures [146]. Similarly to pure Mg samples, the total equivalent hydride layer thickness increases after HPT deformation as shown in Table 4.3. For undeformed ZK60 absorption stops at $t_{MgH_2} = (285.7 \pm 0.8)$ nm. In contrast, an equivalent thickness of $t_{MgH_2} = (471 \pm 2)$ nm is reached for HPT-ZK60. These results will be further discussed in section 5.3, also in relation to the electrochemical loading results.

Figure 4.22 shows the results of the JMAK analysis, while the calculated exponents are reported in Table 4.3. Undeformed ZK60 shows a JMAK exponent between 0.97 and 0.78, which decreases gradually for the subsequent loading steps similarly to undeformed Mg. The n values are

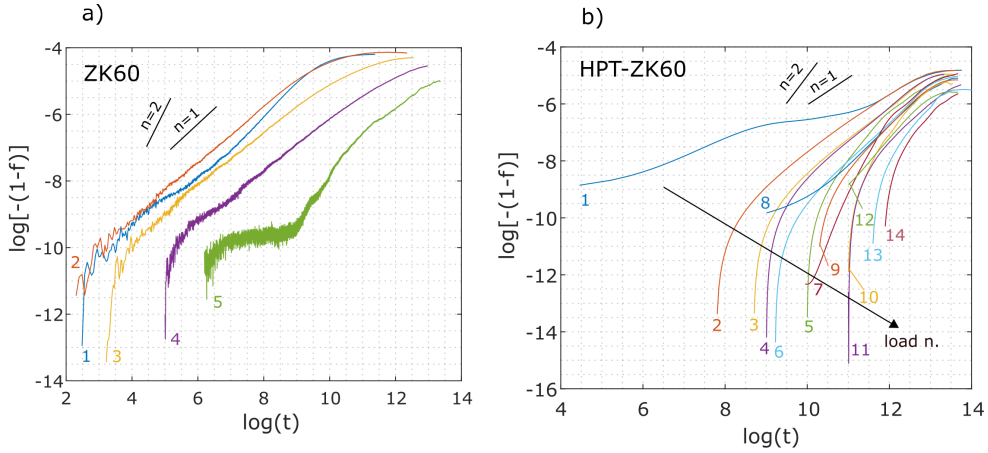


Figure 4.22: JMAK analysis for a) as-extruded ZK60 discs for loading 1 to 5 and b) HPT-ZK60 discs for loading 1 to 14. Lines with a slope of $n = 1$ and $n = 2$ are added as a guide; the fitted exponents are reported in Table 4.3.

similar to those of undeformed Mg and to literature values at higher temperatures for ZK60. For example, at 623 K Avrami exponents between 0.8 and 1.2 were reported in Ref. [146, 147].

For HPT-deformed ZK60, several curves are not linear enough to be fitted in the JMAK model (see Table 4.3), indicating that the one-step model is less suitable to describe the experimental results. The fitted curves exhibit increasing exponents, in the range between 1.1 and 1.86.

4.5.2 Hydrogen loading at 398.2 K

Gas-phase hydrogen absorption was also studied at 398.2 K, to investigate whether the microstructure effects observed at room temperature persist also at higher temperatures. The higher diffusion coefficient expected at this temperature (see section 2.3.6) allows for a larger diffusion range compared to room temperature absorption. This specific temperature was chosen to be above room temperature, but still lower than the often studied temperature of about 570 K (see section 2.3.9). Loading temperature effects were studied for ZK60, where the finest microstructure is reached after HPT, as presented in section 4.1. Moreover, cyclic loading was performed to see how the hydrogen capacity evolve beyond the first absorption.

The setup for gas loading at 398.2 K was introduced in section 3.5.2. When working with an oven in combination with a pressure sensor with no internal temperature control, sensor drift has to be carefully examined. In fact, variations in ambient temperature affect the zero-point of the barometer, resulting in a variation of the recorded pressure over time (drift) according to the manufacturer [210]. Although the pressure sensor is located outside of the oven, it is subjected to

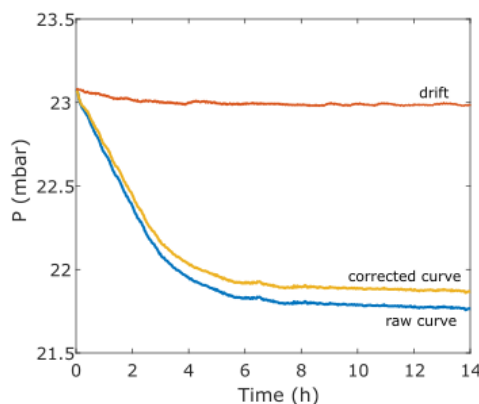


Figure 4.23: orange: sensor drift for a pressure of ~ 23 mbar, using the setup in Figure 3.9 with no sample. blue: representative absorption curve from a Mg sample. yellow: absorption curve corrected by subtracting the sensor drift. The oven temperature was set at 398.2 K. A small drift is observed due to temperature variations of the sensor, which has to be subtracted from experimental absorption isotherms.

ambient temperature variations because of the heat emitted by the oven in the surrounding environment during prolonged use. This effect was therefore monitored, and the measured absorption curves were corrected by subtracting the sensor drift as showed in Figure 4.23. The sensor drift was measured by preparing the loading chamber according to section 3.5.2, setting the pressure to ~ 20 mbar and measuring its variation over time without inserting any sample. The curve was then fitted with a smoothing spline to minimize noise and subtracted from the experimental absorption curves to eliminate drift effects from the experimental data. Although some drift is observed, this effect is small compared to the pressure drop related to hydrogen absorption in the sample.

Before absorption, the discs were coated with Pd and prepared according to section 3.1. Absorption and desorption curves for as-extruded and HPT-deformed ZK60 discs, corrected according to the explained procedure, are reported in Figure 4.24. The experimental procedure for loading and unloading is presented in section 3.5.2. For better comparison, the difference ΔP between the recorded pressure and its initial value is reported. All curves were measured for starting values close to 23 mbar. This value was obtained by setting a pressure of 40 mbar in the whole experimental setup excluding the sample chamber, and subsequently opening the valve to let the hydrogen gas in the sample chamber at the start of the measurement (see Figure 3.9). For unloading, no drift correction was performed. The measured values are also less precise because the pressure is not recorded in the initial phases of unloading, while the valve is opened to evacuate the loading chamber. Nonetheless, the pressure changes during absorption and desorption are close to each other and a flat desorption curve is always achieved, meaning that the unloading process was carried to completion before starting the following loading step.

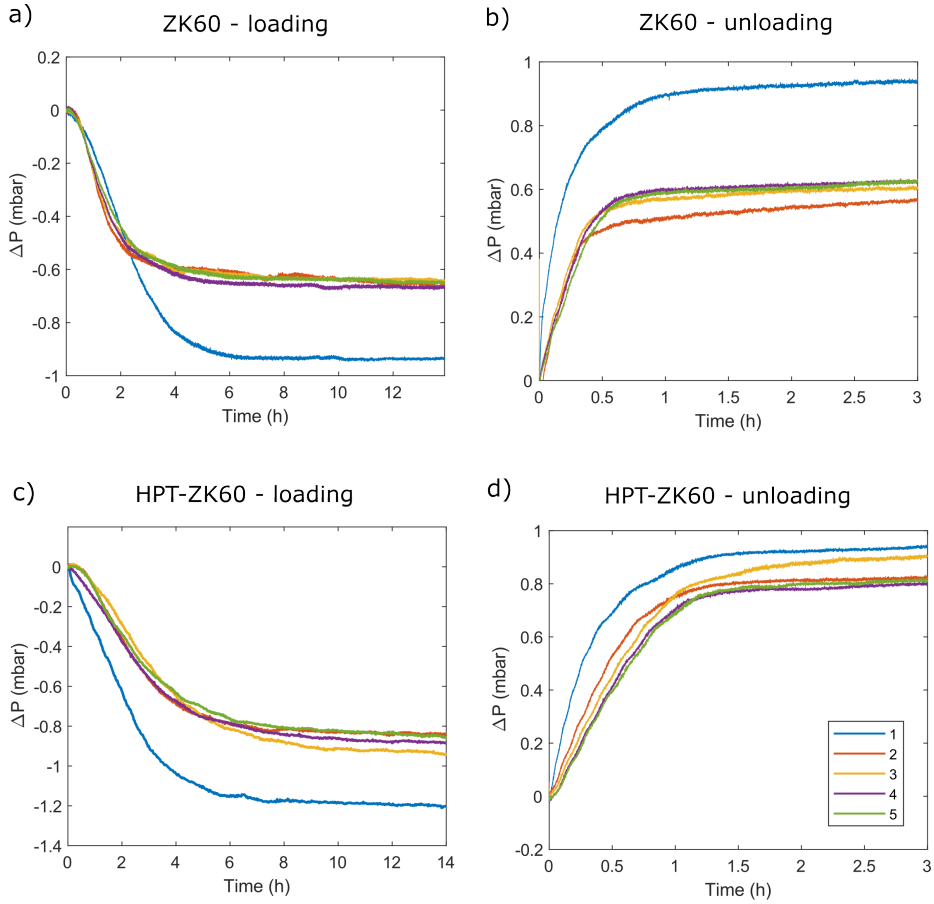


Figure 4.24: Hydrogen gas absorption and desorption curves recorded at 398.2 K for a) undeformed ZK60 discs (loading), b) undeformed ZK60 discs (unloading), c) HPT-deformed ZK60 discs (loading), d) HPT-deformed ZK60 discs (unloading). All absorption curves show an incubation time of about 40 min, excluding the first hydrogenation of HPT-ZK60. For both samples, the pressure drop is largest for the first hydrogenation and then decreases starting from the second hydrogenation; a constant pressure drop is maintained from the second to the fifth hydrogenation. Desorption is faster than absorption.

Table 4.4: Moles of hydrogen absorbed n_H according to Eq. 3.8, equivalent hydride thickness d_{MgH_2} according to Eq. 3.1 and time necessary to reach 90% of the final absorbed hydrogen quantity for Pd-coated ZK60 (see Figure 4.24.a) and HPT-ZK60 (see Figure 4.24.c).

Sample	Load n.	n_H (10^{-5} mol)	Eq. t_{MgH_2} (μm)	$t_{90\%}$ (h)
ZK60	1	1.24 ± 0.03	1.43 ± 0.04	4.12
	2	0.87 ± 0.10	1.00 ± 0.02	3.5
	3	0.84 ± 0.09	0.97 ± 0.02	3.6
	4	0.88 ± 0.02	1.02 ± 0.03	3.7
	5	0.86 ± 0.02	0.99 ± 0.02	3.9
HPT-ZK60	1	1.58 ± 0.04	1.50 ± 0.04	4.5
	2	1.11 ± 0.03	1.05 ± 0.03	5.2
	3	1.22 ± 0.03	1.17 ± 0.03	6.5
	4	1.16 ± 0.03	1.10 ± 0.03	6.1
	5	1.12 ± 0.03	1.07 ± 0.03	6

The absorption and desorption cycle was repeated for 5 times for the two different samples. Figure 4.24.a shows the five absorption cycles for undeformed ZK60 coated with Pd. For each cycle, the moles of hydrogen absorbed according to Eq. 3.8 and the equivalent hydride thickness according to Eq. 3.1 are reported in Table 4.4. As visible in Figure 4.24.a, in the first cycle a larger pressure drop is observed, which is related to a higher number of absorbed hydrogen moles and to an equivalent hydride thickness of $1.4 \mu\text{m}$. For cycles 2 to 5, the absorption curves overlap and no further change in capacity is observed. The amount of absorbed hydrogen decreases from $1.24 \cdot 10^{-5}$ mol in the first loading cycle to $0.84 - 0.88 \cdot 10^{-5}$ mol in the following cycles, corresponding to a reduction of 32% to 29% relative to the first loading cycle. To characterize the absorption time, Table 4.4 reports the time necessary to achieve 90% of the final capacity, which remains close to 4 hours. The desorption time is also consistent within the different cycles and is below 1.5 hours, as can be seen in Figure 4.24.b. A faster desorption compared to absorption is common at temperatures close to 570 K for SPD-ZK60 [9, 14, 15, 147, 151, 211] and other Mg-based materials [10, 155, 212].

Similarly to what is observed in as-extruded ZK60, also for the sample deformed by HPT the first absorption is associated to a larger pressure drop, as shown in Figure 4.24.c. The absolute pressure drop is larger compared to the first absorption for undeformed ZK60. However, once the larger surface area of HPT samples compared to as-extruded discs is accounted for, the equivalent hydride thickness is only slightly larger, changing from $1.43 \mu\text{m}$ to $1.5 \mu\text{m}$. Also here, a reduction in the absorbed amount of hydrogen is observed for cycles 2 to 5 (see Table 4.4), with 22% to 30% less hydrogen absorbed compared to the first cycle. This variation in hydrogen capacity will be further discussed in section 5.4. The absorption times are slightly larger for

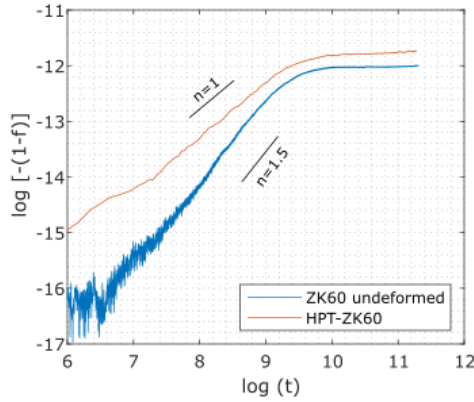


Figure 4.25: JMAK curve for the first absorption of undeformed and HPT-ZK60.

HPT-ZK60 than for the undeformed sample, and increase from 4.5 hours in the first absorption to 6 hours for the last loading cycle. The desorption times are consistent within the different cycles and below 1.5 hours. A different shape of the absorption curves can also be observed in Figure 4.24.c, where the first absorption curve is faster in the initial stage and does not show a slower portion at the beginning, unlike for the following cycles and for undeformed ZK60, this is also further discussed in section 5.4.

Similarly to the room temperature absorption, a JMAK analysis was performed according to section 3.5.3. For both undeformed and HPT-deformed ZK60, only the first loading cycle produced a linear JMAK curve, which is reported in Figure 4.25. Fitting the curve according to Eq. 3.9, we obtain an Avrami exponent of 1.508 ± 0.002 for the undeformed sample and of 0.989 ± 0.008 for HPT-deformed ZK60. The obtained exponents are close to those observed at room temperature.

4.6 Positron Annihilation Spectroscopy (PAS)

Positron annihilation spectroscopy studies were performed on ZK60 samples according to section 3.7, in collaboration with Prof. J. Cizek, Charles University Prague. Positron lifetime studies allow to calculate the dislocation density along the sample's radius (section 4.6.1), while coincidence Doppler broadening measurements characterize the chemical environment of dislocations (section 4.6.2) including the distribution of the Zn and Zr alloying elements.

4.6.1 Positron Lifetime Investigations

The results of positron lifetime investigations are summarized in Table 4.5. The virgin sample of the ZK60 alloy exhibits a single-component positron lifetime spectrum, with a lifetime $\tau_1 = (223.6 \pm 0.2)$ ps. This value aligns well with the bulk positron lifetime for magnesium [213], indicating that the virgin sample contains a low concentration of defects, and all positrons are annihilated while being in a free, delocalized state within the lattice.

Table 4.5: Results of positron lifetime investigations of ZK60 samples: lifetimes τ_i and intensities I_i of the components resolved in positron lifetime spectra.

ZK60 sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
virgin	223.6 ± 0.2	100	-	-
HPT-deformed, $r = 0$ mm	213 ± 2	53 ± 4	240 ± 2	47 ± 5
HPT-deformed, $r = 1.5$ mm	210 ± 2	44 ± 3	238 ± 2	56 ± 5
HPT-deformed, $r = 3$ mm	202 ± 2	35 ± 3	241 ± 2	65 ± 5

In contrast, the positron lifetime spectra of HPT-deformed samples consist of two components. The shorter component, with lifetime τ_1 , corresponds to free positrons. The longer lifetime component τ_2 reflects positrons trapped at defects introduced by HPT processing. The value of τ_2 , which is around 240 ps, is similar to reported values for positrons trapped at dislocations in Mg alloys [213–215]. This suggests that, in HPT-deformed samples, a fraction of positrons is trapped at dislocations created by severe plastic deformation.

The positrons lifetimes in samples containing dislocations are slightly shorter than the positron lifetimes at monovacancies [216]. It should be noted that the dislocation line itself acts as a shallow positron trap. A positron that is weakly localized within the dislocation line can rapidly diffuse along it and eventually move to a deep trap associated with the dislocation, where it will then be annihilated [217]. The deep traps associated to dislocation are identified with vacancies on the dislocation line [218] or by jogs in the dislocation line [218–220], which form following the intersection of moving dislocations. Both types of defects have been associated with slightly shorter positron lifetimes compared to monovacancies using molecular dynamics simulations [218]. In the case of a vacancy on the dislocation line, this can be understood intuitively since the vacancy is distorted and has a smaller volume compared to a vacancy in the perfect lattice, leading to a faster annihilation of the trapped positron.

The intensity I_2 of the component related to positrons trapped at dislocations increases with the radial distance r from the center of the sample. This is because, in torsion deformation, the strain escalates with increasing distance from the axis of rotation as introduced in section 2.2.1.

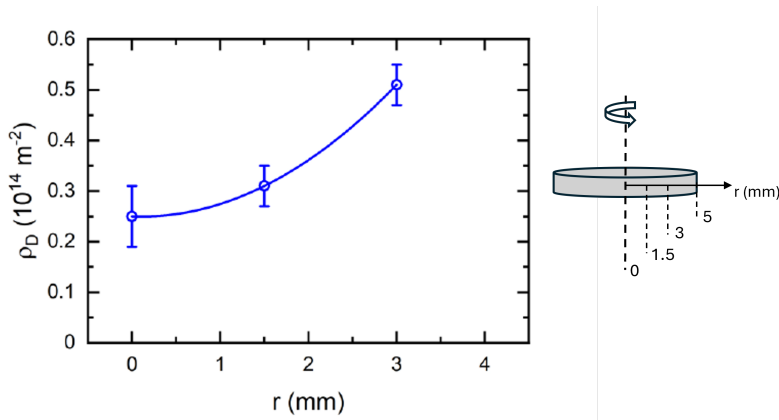


Figure 4.26: Dislocation density calculated from positron lifetime data using Eq. 3.17 plotted as a function of the radial distance r from the center of sample disc. The dislocation density increases when moving from the center of the sample towards its edge.

Note that the quantity $\tau_f = (I_1/\tau_1 + I_2/\tau_2)^{-1}$ (see Eq. 3.16), derived from positron lifetime spectroscopy data for samples subjected to HPT, aligns within experimental uncertainty with the bulk positron lifetime for magnesium. This finding supports the validity of the two-state simple trapping model (STM) introduced in section 3.7.1. As a result, the STM can be employed to determine the concentration of defects according to Eq. 3.17. Here, we used the specific trapping rate for defects associated to dislocations in Mg $v_d = 10^{-5} \text{ m}^2\text{s}^{-1}$ as reported in ref. [215]. The density of dislocations calculated using Eq. 3.17 is plotted in Figure 4.26, clearly demonstrating an increase with the radial distance r from the center of the sample disc.

As Figure 4.26 shows, the measured dislocation density increases from $\sim 2.5 \times 10^{13} \text{ m}^{-2}$ at the center of the sample to $\sim 5 \times 10^{13} \text{ m}^{-2}$ at $r = 3 \text{ mm}$. These values are almost one order of magnitude lower than literature values for the dislocation density in HPT-ZK60 deformed at room temperature, which are between $3 \times 10^{14} \text{ m}^{-2}$ and $7 \times 10^{14} \text{ m}^{-2}$ [146, 206]. These literature values were obtained by XRD, evaluating the broadening of diffraction peaks. A similar discrepancy between dislocation density values obtained by PAS and XRD has already been reported for a Mg-Al-Zn alloy deformed by ECAP [215], although for both methods the same dependency of the dislocation density on the number of ECAP passes was observed. Both experimental methods contain assumptions; for PAS, in particular, the trapping rate for dislocation v_d cannot be measured experimentally but it must be calculated from first principle models [215]. The discrepancy between PAS and XRD could also be caused by the different probed depth in the sample: while PAS probes the whole sample thickness, the x-ray diffraction signal only comes from a depth of a few micrometers below the sample's surface [215]. Therefore, if the dislocation density varies along the rotation axis (perpendicular to the disc's surface), XRD may be less precise in determining the global dislocation density. In conclusion, the discrepancy between the PAS

results and the XRD literature values does not invalidate the observed increase of dislocation density along the radius of the disc. However, we cannot exclude that the absolute value of the dislocation density may be underestimated.

4.6.2 Coincidence Doppler Broadening (CDB) Investigations

The CDB ratio curves for ZK60 samples studied are plotted in Fig. 4.27. The ratio curves for all samples are similar and exhibit minima at $p \approx 6.5 \times 10^{-3} m_0c$ followed by a peak located at $p \approx 11 \times 10^{-3} m_0c$. HPT deformation results in an increase of the contribution in the low momentum range due to the creation of dislocations and a slight increase of the peak at $p \approx 11 \times 10^{-3} m_0c$. The high-momentum region of the curves is related to positron annihilating with core electrons in Mg, Zn or Zr atoms, while the low-momentum area is related to positron annihilating with valence electrons [196]. Positron trapping at lattice defects decreases the overlap between the positron probability density and the probability density of core electrons, and in turn increases the fraction of positrons annihilating with valence electrons, generating a higher contribution in the low-momentum region of the CDB spectra [214].

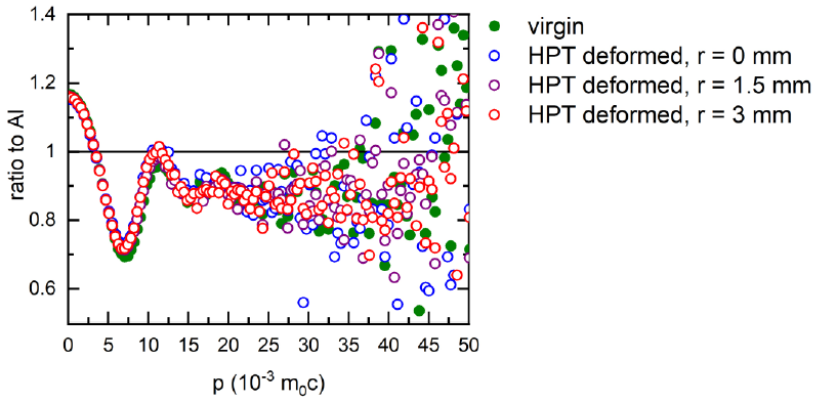


Figure 4.27: CDB ratio curves (related to well annealed pure Al) for ZK60 samples. HPT deformation increases the signal in the low-momentum region.

The ZK60 alloy consists of Mg with an addition of 6 wt.% Zn and 0.5 wt.% Zr. In terms of atomic percentages, this corresponds to a composition of 97.6 at.% Mg, 2.3 at.% Zn and 0.14 at.% Zr. The momentum distribution of positron-electron pairs that annihilate in ZK60 alloys

can be described in the high momentum region as a superposition of the curves for the contained elements Mg, Zn, and Zr [214].

$$n(p) = (1 - F_d) \sum_X \xi_{X,f} n_{X,f}(p) + F_d \sum_X \xi_{X,d} n_{X,d}(p) \quad (4.1)$$

where $X = Mg, Zn, Zr$, while $n_{X,f}(p)$ and $n_{X,d}(p)$ denote the momentum distribution of free positrons and positrons trapped at defects, respectively, annihilated by core electrons belonging to the element X . The coefficients $\xi_{X,f}$ represent relative fractions of free positrons annihilated by core electrons of each element, normalized so that $\sum_X \xi_{X,f} = 1$. Similarly, the coefficients $\xi_{X,d}$ correspond to relative fractions of positrons trapped at dislocations and annihilated by core electrons belonging to each element. These coefficients are also normalized so that $\sum_X \xi_{X,d} = 1$. The symbol F_d stands for the fraction of positrons annihilated in trapped state at defects.

Figure 4.28 illustrates a comparison of CDB ratio curves for ZK60 samples alongside the ratio curves $n_{X,f}(p)$ and $n_{X,d}(p)$ of pure elements $X = Mg, Zn, Zr$.

The ratio curves associated with free positrons $n_{X,f}(p)$ were obtained from well-annealed samples of these pure metals, where all positrons annihilate in the free state. The ratio curves $n_{X,d}(p)$ were obtained by measuring heavily cold rolled samples of pure metals Mg, Zn and Zr. In heavily cold rolled reference samples, a significant fraction of positrons is trapped at dislocations introduced by plastic deformation. Hence, for cold the rolled reference sample of element X the momentum distribution of electron-positron annihilating pairs can be expressed as:

$$n(p) = (1 - F_d) n_{X,f}(p) + F_d n_{X,d}(p) \quad (4.2)$$

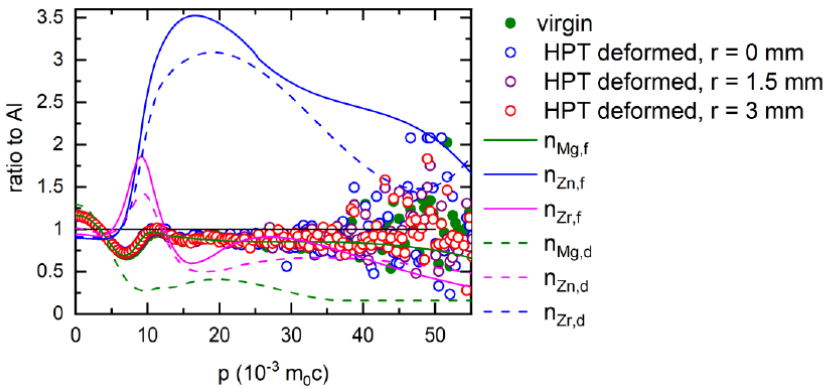


Figure 4.28: Comparison of CDB ratio curves (related to well annealed pure Al) for ZK60 samples and reference samples $n_{X,f}(p)$ (solid lines) and $n_{X,d}(p)$ (dashed lines) for pure elements $X = Mg, Zn, Zr$. As expected from the chemical composition of the alloy, the largest contribution is related to positron annihilation in Mg.

The momentum distribution $n_{X,f}(p)$ was assessed by measuring well annealed samples, and the fraction F_d of positrons trapped at dislocations was determined from positron lifetime measurements of the cold rolled sample within STM introduced in paragraph 3.7.1:

$$F_d = I_2 \left(1 - \frac{\tau_1}{\tau_2} \right) \quad (4.3)$$

where τ_1 is the lifetime of the free positron components, τ_2 is the lifetime of positrons trapped at dislocations, and I_2 is the intensity of this component. Combining Eq. 4.2 and 4.3, the momentum distribution $n_{X,d}$ can be calculated as:

$$n_{X,d}(p) = \frac{n(p) - (1 - F_d)n_{X,f}(p)}{F_d} \quad (4.4)$$

From an analysis of Fig. 4.28, it can be concluded that the CDB ratio curves measured for the ZK60 samples are similar to the reference curve $n_{Mg,f}(p)$ for well-annealed pure Mg, as can be expected since the ZK60 samples contain more than 97 at.% Mg and the majority of positrons is annihilated in the free state (see Table 4.6).

For the virgin ZK60 sample, all positrons are annihilated in the free state, i.e. $F_d = 0$, meaning that 4.1 simplifies to:

$$n(p) = \sum_X \xi_{X,f} n_{X,f}(p) \quad (4.5)$$

Fig. 4.29 shows CDB ratio curve for the virgin ZK60 sample together with the best fit using Eq. 4.1. Clearly the model function provided by Eq. 4.1 describes the experimental points accurately. From fitting we obtained the coefficients listed in Table 4.6. The coefficients $\xi_{Zn,f}$ and $\xi_{Zr,f}$ are smaller than the atomic concentrations of Zn and Zr in ZK60 alloys. This indicates that α -Mg matrix of the virgin ZK60 alloy, which is probed by free positrons, is depleted in Zn and Zr. This agrees with the results from section 4.1.2, showing how significant fractions of Zn and Zr atoms form intermetallics, instead of being solved in the hcp magnesium matrix. These aspects are further discussed in section 4.7 in comparison to TEM and SEM results.

For the HPT-deformed samples, the fraction of positrons trapped at dislocations was calculated from the positron lifetime measurements according to Eq. 4.3. The fractions of positrons trapped at dislocations are summarized in Table 4.6. The HPT-deformed sample measured at the margin ($r = 3 \text{ mm}$) shows the highest fraction of positrons annihilated at dislocations because it contains the highest density of dislocations. However, in this sample, the fraction of positrons trapped at dislocations is only $F_d = 0.11$. The other positions exhibit even smaller values, suggesting that

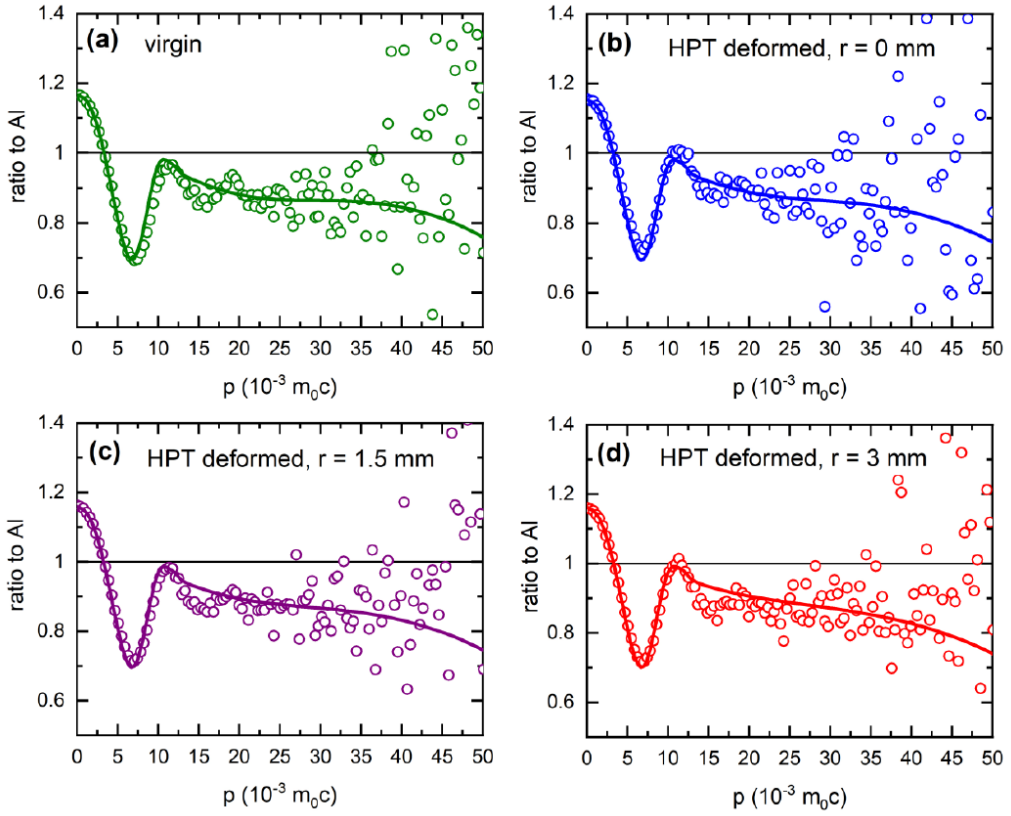


Figure 4.29: Results of fitting of CDB ratio curves (related to well annealed pure Al) for ZK60 samples in the virgin state (a) and after HPT deformation measured in the center of the sample disc (b) and in the radial distance $r = 1.5$ mm (c) and $r = 3$ mm (d). Solid lines are model curves calculated using Eq. 4.5 for the virgin sample and Eq. 4.1 for HPT deformed samples.

Table 4.6: Results of fitting of CDB ratio curves for ZK60 samples by superposition of the curves for pure elements using Eq. 4.1. The fraction F_d of positrons trapped at dislocations was calculated from positron lifetime data using Eq. 4.3.

ZK60 sample	F_d	$\xi_{Zn,f}$	$\xi_{Zr,f}$	$\xi_{Zn,d}$	$\xi_{Zr,d}$
virgin	0	0.005 ± 0.001	0.0014 ± 0.008	-	-
HPT, $r = 0$ mm	0.05 ± 0.01	0.005	0.0014	0.29 ± 0.05	0.23 ± 0.06
HPT, $r = 1.5$ mm	0.07 ± 0.01	0.005	0.0014	0.24 ± 0.03	0.30 ± 0.05
HPT, $r = 3$ mm	0.11 ± 0.01	0.005	0.0014	0.25 ± 0.02	0.26 ± 0.04

the contribution from positrons trapped at dislocations represents only a minor part of the concurrent CDB ratio curves, while the predominant contribution comes from positrons annihilating in the free state.

In fitting of CDB ratio curves for HPT deformed samples we used Eq. 4.1 and the coefficients $\xi_{X,f}$ were fixed at the values determined for the virgin sample, since the chemical composition of the α -Mg matrix should not change by HPT processing. Thus, the only fitting parameters are the coefficients that describe the local chemical environment of dislocations in HPT-deformed ZK60 samples. Results of fitting of CDB ratio curves of HPT-deformed are presented in Figs. 4b-4d. In all cases, the model curves calculated using Eq 4.1 describe the experimental points accurately. The coefficients obtained from fitting are summarized in Table 4.6. It is evident that the chemical environment of dislocations in HPT-deformed ZK60 samples is enriched with Zn and Zr atoms, as the coefficients are significantly higher than the atomic concentrations of these elements in ZK60 alloy. This indicates a segregation of Zn and Zr solutes at the dislocations.

4.7 In-situ TEM H loading

The formation of magnesium hydride in ZK60 samples was studied by in-situ TEM hydrogen loading in collaboration with Dr. S. Korneychuk (IAM-WK, KIT), using an atmosphere holder as described in section 3.2. A palladium-coated lamella was used in these studies; a natural layer of magnesium oxide shields the sample from hydrogen absorption at the sides. These results help clarifying issues emerging in the previous sections. Hydrogen absorption was studied at room temperature for HPT-ZK60 to visualize the formation of the magnesium hydride blocking layer and determine the time scale for hydrogen absorption, in comparison with the results from gas-phase loading in section 4.5.1. Hydrogen absorption was also observed for HPT-ZK60 at 398.2 K under a pressure of 20 mbar H_2 , similarly to the bulk measurements in section 4.5.2, to better target the kinetics of hydride formation and compare the achieved hydride thickness. Absorption and desorption cycles were also performed on undeformed ZK60 samples, to better understand the variations in hydrogen capacity observed during absorption/desorption cycling of bulk samples in section 4.5.2. Moreover, EDX observation are compared to the SEM and PAS results in sections 4.1 and 4.6.

Figure 4.30 shows a HPT-ZK60 sample before hydrogen loading. A STEM HAADF image is reported in Figure 4.30.a. Bright particles are inhomogeneously distributed in the observed area. By the EDS map in Figure 4.30.c, it can be seen that the bright particles are associated to an increased Zn content. They can be identified with precipitates of the intermetallic phase $MgZn_2$, which was observed for ZK60 samples by XRD (see section 4.2). Similar precipitates were observed also in SEM images of both undeformed and HPT-deformed ZK60 (see section 4.1.2),

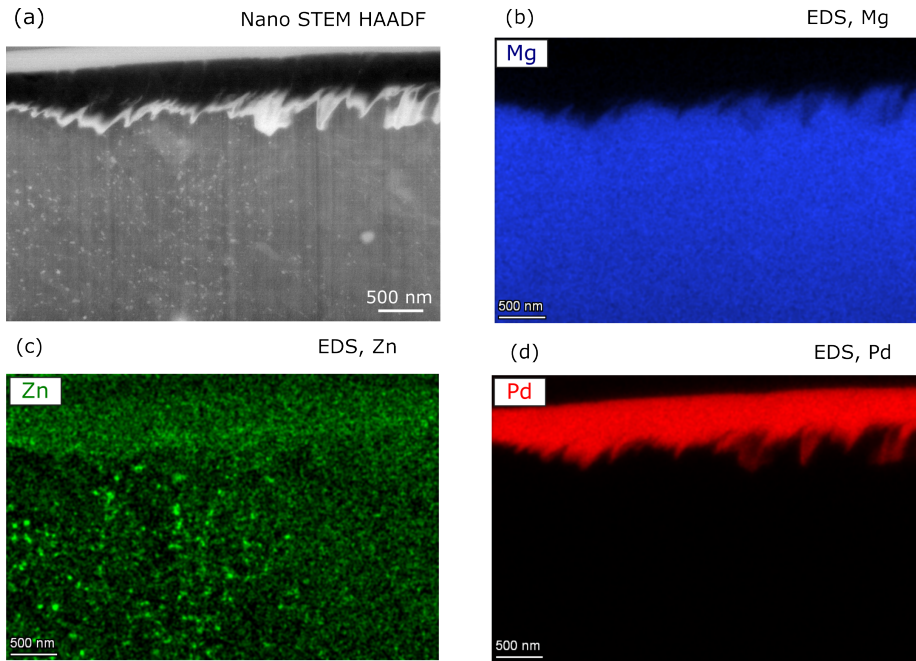


Figure 4.30: TEM micrographs of a Pd-coated ZK60 sample deformed by HPT before in-situ TEM hydrogen loading. (a): NANO STEM HAADF image, (b) Mg spatial distribution by EDS (net), (c) Zn spatial distribution by EDS (net), (d) Pd spatial distribution by EDS (net). A closed palladium coating is observed on the sample's surface. The bright particles visible in panel a) are associated to an increased concentration of Zn. The rough surface is caused by the sample preparation described in section 3.2.

although their chemical composition could not be identified due to their small size. Moreover, positron CDB measurements highlighted that Zn and Zr are depleted in the α -Mg matrix of ZK60, which can be explained by their concentration in second-phase precipitates (see section 4.6.2). Together with MgZn_2 , the Zn_2Zr phase is also expected from the phase diagram in Figure 2.2. An enrichment in Zn and Zr, together with a Mg depletion, was observed for bright particles in the micrometer range in SEM images (see Figure 4.5), which are not present in the area studied in the TEM. This is attributed to their low overall volume content.

As expected, α -Mg is uniformly present in the whole studied area (Figure 4.30.b). The coating Pd layer is visible in Figure 4.30.d. Although the Mg-Pd interface is not smooth, Pd forms a continuous and closed layer on top of the magnesium sample, which is still intact after HPT deformation. The roughness of the interface is due to the preparation of the magnesium surface, which was only grinded with a 4000 grit paper before coating it with Pd, to avoid the surface contamination caused by polishing with diamond suspensions and Etosil E, as shown in section 4.1.

After this initial characterization, the sample was loaded with hydrogen. For the first measurement, the sample was exposed to a pressure of $p_{H_2} = 6.67$ mbar at a temperature of 298.15 K. This value is higher than the 0.1 mbar used for room-temperature gas-phase loading of bulk samples, and was used because it was the lowest pressure which could be applied through the TEM atmosphere holder. Figure 4.31.a shows the resulting EELS map after 12 h. It can be seen that a closed hydride layer of around 200 nm has formed, starting from the Pd-Mg interface. This indicates that hydrogen is absorbed in the lamella through the Pd capping layer, and not directly from the exposed Mg sides, and may indicate the presence of a Mg-oxide layer on the TEM lamella sides which can form quickly during transportation of the sample. This procedure has been successfully used by Hamm et al. on Pd-coated Mg lamella which were only hydrogenated from the Pd surface [115]. Moreover, given the high barrier to H_2 dissociation on Mg surfaces (see section 2.3.1), it is unlikely to observe hydrogen gas absorption in non-coated magnesium at room temperature. This loading modality represents the experimental conditions of bulk samples, where hydrogen can only penetrate the sample through the Pd capping layer. Therefore, the results from TEM in-situ loading can be compared to H loading in bulk samples, which would not be possible if hydrogen were absorbed directly from the Mg surface. In some positions the hydride extends deeper, reaching ~ 600 nm from the interface with the capping layer. This aspect is further discussed in section 5.3.

After loading, the absorbed hydrogen was removed by decreasing the atmosphere holder hydrogen pressure. As Figure 4.31.b shows, the areas which were previously occupied by magnesium hydride now contain a high density of pores, while the rest of the sample remains unaffected. Interestingly, pore formation was not only observed at room temperature for ZK60 samples. Figure 4.32 shows a loading experiment for an undeformed ZK60 lamella. The sample was loaded with hydrogen for 30 min at 373.15 K, applying a pressure of $p_{H_2} = 266$ mbar, subsequently it was unloaded by decreasing the hydrogen pressure and maintaining a constant temperature. Also in this case, pores appear after the decomposition of the hydride phase, as can be seen in Figure 4.32.b. Subsequently, the sample was loaded with hydrogen a second time at 423.15 K for 1 h, under a pressure of $p_{H_2} = 400$ mbar. The pressure-temperature combinations were chosen to be slightly above the equilibrium pressure for hydride formation according to the van't Hoff plot in Figure 2.16. In this way, the overpressure provides a driving force for magnesium hydride formation. During the second loading the pores are no longer visible, with the exception of some areas close to the Mg-Pd interface. This might be explained by the expansion of the surrounding magnesium volume following hydride formation.

Finally, the HPT-ZK60 lamella was loaded a second time at 398.2 K under a hydrogen pressure of 20 mbar. This pressure-temperature combination was chosen to be comparable with the experimental results on bulk ZK60 in section 4.5.2. Since the equilibrium pressure at 398.2 K is close to 2 mbar (see Figure 2.16), an overpressure of 20 mbar provides an appropriate driving

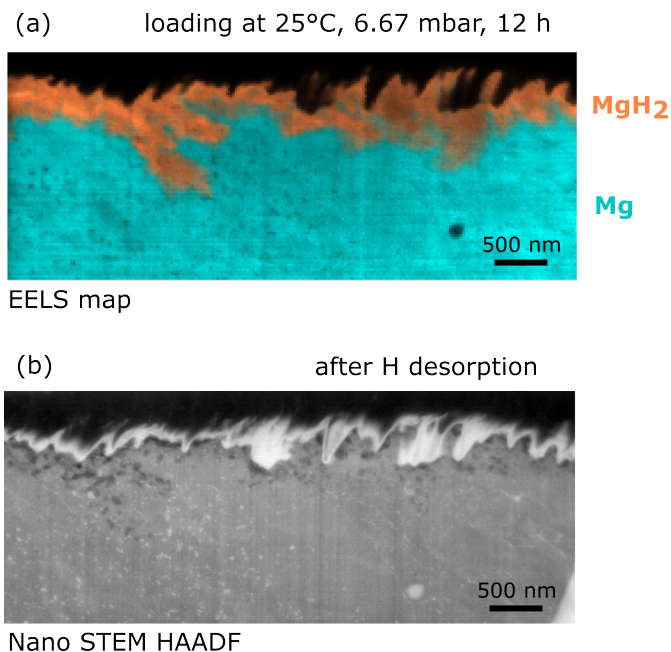


Figure 4.31: TEM micrographs for in-situ TEM hydrogen loading and unloading at room temperature for a Pd-coated HPT-ZK60 sample. (a) EELS map for magnesium hydride and α -Mg after loading for 12 h at 298.15 K under a hydrogen pressure of 6.67 mbar. (b) STEM HAADF image of the unloaded sample after removing the hydride layer. A closed hydride layer of around 200 nm is formed after 12 h. After dehydrogenation, pores are visible in the region that previously contained magnesium hydride.

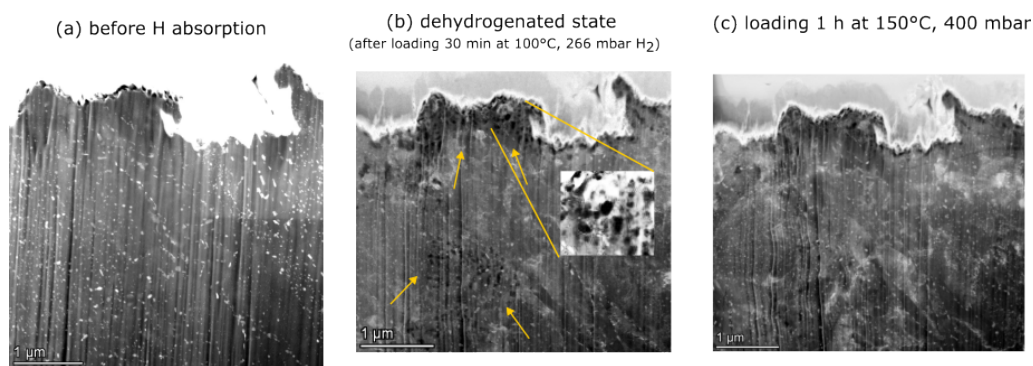


Figure 4.32: STEM HAADF images of one undeformed ZK60 sample coated with Pd in different hydrogenation states. (a) before hydrogen loading. (b) after loading for 30 min at 373.15 K under a hydrogen pressure of 266 mbar, and subsequently unloading by removing the hydrogen atmosphere and maintaining the temperature. Pores are visible after unloading, indicated by yellow arrows. Some of the pores are made more visible in the inset with increased contrast. (c) after loading for 1 h at 423 K under a hydrogen pressure of 400 mbar. The pores which appeared after dehydrogenation are partly closed in this second loading, with the exception of some areas close to the Pd-coated surface. The visible vertical stripes are related to a curtaining effect during Ga-ion milling.

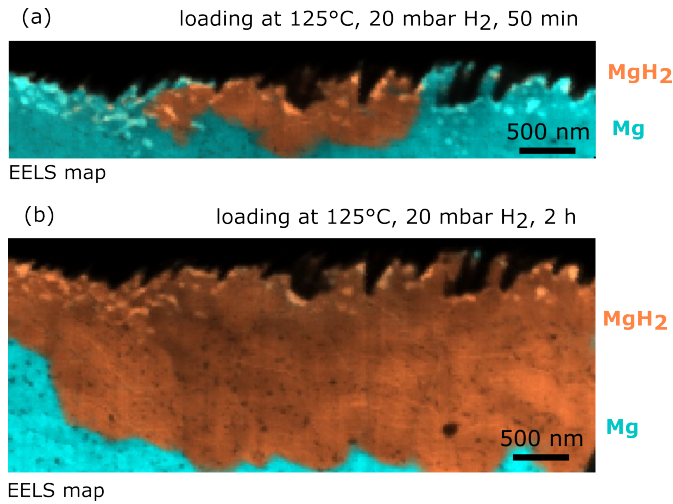


Figure 4.33: Results for in-situ TEM hydrogen loading at 398.2 K for a Pd-coated HPT-ZK60 sample. (a) EELS map for magnesium hydride and α -Mg after loading for 50 min at 398.2 K under a hydrogen pressure of 20 mbar. (b) EELS map for magnesium hydride and α -Mg after loading for 2 h at 398.2 K under a hydrogen pressure of 20 mbar. A hydride layer close to $1.5\ \mu\text{m}$ forms after loading for 2 h. A smaller region is hydrided in the first 50 min compared to the second half of the experiment.

force to hydride formation. Figure 4.33 shows the EELS maps of the second H loading at two different time stamps. After 50 min (Figure 4.33.a) only a small area is hydrided, extending less than 500 nm from the Mg-Pd interface. After 2 h (Figure 4.33.b) the hydride phase has extended to a depth of $\sim 1.5\ \mu\text{m}$. These results are further discussed in section 5.4, also in comparison with the hydrogenation experiments performed on bulk ZK60 samples.

5 Discussion

The main objective of this work was to understand how HPT-induced microstructures affect hydrogen kinetics in Mg and ZK60 samples at different temperatures. Firstly, the microstructure resulting from HPT is discussed in section 5.1. Different microstructural aspects can affect different steps of hydride formation kinetics in magnesium. The main kinetics steps for the magnesium-hydrogen system include hydrogen dissociation on the magnesium surface, hydride nucleation and hydrogen transport in the hydride phase and at grain boundaries. Especially, grain boundaries are suggested to act as fast transport channels, being present in high quantity in HPT processed samples. Hydride nucleation and hydrogen transport at grain boundaries were tackled at room temperature with different experimental techniques, whose results are discussed in section 5.2 and 5.3. It emerges that hydride nucleation is mostly affected by the presence of intermetallic phases, while transport at grain boundaries affects the global hydrogen capacity. Effects related to texture emerge by cyclic loading at 398.2 K, as discussed in section 5.4. The evolution of the microstructure during cyclic loading and its effects on hydrogen absorption are also discussed in section 5.4. Since the samples are coated with palladium, the effects of hydrogen dissociation on absorption kinetics are minimized in this work, allowing for an interesting comparison with studies performed without coating, where surface effects play a major role in hydrogen absorption kinetics.

5.1 Deformation mechanisms during HPT for Mg and ZK60

The mechanisms of microstructure refinement following plastic deformation of Mg and Mg-alloys have been introduced in section 2.1.1, and are here related to the experimental results of section 4.1.

For magnesium, an extremely coarse microstructure is observed for as-extruded discs, with grains in the mm range. After HPT, the grain size is reduced to $\sim 790\text{ nm}$, with larger grains close to $1\text{ }\mu\text{m}$ visible especially in the center of the sample (see section 4.1.1). As discussed in section

2.1.1, plastic deformation in magnesium with such coarse grains results initially in twinning-associated dynamic recrystallization, followed by low temperature continuous dynamic recrystallization (LTDRX). This is the driving force for the observed final microstructure of the samples, possessing grains below the micrometer range, achievable by LTDRX. Hence, the combination of HPT and LTDRX results in the desired grain refinement.

In detail, Figueiredo and Langdon [70, 71] proposed for HPT deformation of magnesium-alloys a mechanism similar to ECAP deformation, with new finer grains nucleating close to grain boundaries and expanding to occupy the center of the original grains. While this mechanism is plausible in the ECAP temperature range of 400 - 600 K (see section 2.2.2), where plastic deformation leads to continuous dynamic recrystallization (CDRX), it seems unlikely at room temperature. In fact, if grain refinement only started close to the grain boundaries, a necklace structure of fine recrystallized grains close to the original grain boundaries would be expected, since the very coarse initial grain size of magnesium would be above the critical size necessary to achieve a uniform microstructure (see also Figure 2.10). The experimental results are more in line with low temperature dynamic recrystallization (LTDRX), where the new finer grains form within the existing grains without a preferred site, as a result of the long range shear strain accumulated in the sample.

Coming to ZK60, the initial grain size is in the 10 μm range, while the refined grains are smaller than 100 nm. According to the LTDRX mechanism, a smaller grain size is expected compared to magnesium due to the effect of alloying elements Zn and Zr, which can stabilize the newly formed low angle grain boundaries and prevent their annihilation. This explains directly the smaller grain size achieved in comparison to HPT-deformed magnesium. In fact, the movement of dislocations in ZK60 at room temperature is hindered primarily by two mechanisms: precipitation hardening and Zn solid-solution hardening [27, 221–223]. According to Nie et al. and Robson et al., precipitation hardening happens because of Mg-Zn precipitates and can be described through the Orowan mechanism [222, 223], where moving dislocation lines bow around precipitates and leave behind dislocation loops. The Zn atoms in solid solution also affect dislocation movement, although in a more complex way. In fact, solute Zn can lead to hardening in the basal plane and at the same time to softening in the prismatic planes [221]. However, it emerges from the PAS measurements that only a small fraction of Zn is in solid solution in hcp Mg, and the largest fraction forms intermetallic precipitates. Therefore, we may expect precipitation hardening to play a more prominent role.

Indeed, an increase in dislocation density was observed by positron annihilation spectroscopy (PAS) as a consequence of HPT (see section 4.6). The dislocation density increases with the distance from the rotation axis of the HPT deformed sample, similarly to the applied shear strain (see Figure 4.26). This observation is also compatible with LTDRX. At higher temperatures, in fact, the newly formed dislocations are firstly consumed to form low angle grain boundaries and

later absorbed by grain boundary sliding, so that no relevant increase in dislocation density is expected at the end of the recrystallization process. On the contrary, at low temperature dislocations cannot be absorbed by HAGBs [59], and tend to accumulate in their vicinity.

To conclude, both for Mg and for ZK60, the observed microstructures are compatible with the proposed mechanism of LTDRX, where the long range shear strain accumulated in the sample leads to the formation of recrystallized grains without preferred nucleation sites, and the produced dislocations cannot be entirely absorbed by the newly formed grain boundaries. For both materials HPT-induced LTDRX results in the desired grain refinement, even though the magnitudes of grain refinement and the final grain sizes are of different orders. For ZK60, the presence of Zn and Zr results in the targeted grain sizes below 100 nm.

5.2 Hydride nucleation and blocking layer formation in Mg and ZK60 at room temperature

Different effects related to the sample's chemical composition, to its microstructure, and to the loading parameters emerge by electrochemical hydrogen loading at room temperature, as reported in section 4.3.2. Here, these effects are further discussed and analyzed.

When interpreting the electrochemical isotherms in section 4.3, the context emerging from FEM diffusion simulations in section 4.4 must be taken into account. As described in section 3.4, during electrochemical loading hydrogen is introduced in the Pd capping layer by applying a defined current density for a 90 s time interval to the sample's surface. Afterwards, hydrogen is left to diffuse into the sample for 30 min, to achieve thermodynamic equilibrium. Whether this waiting time is appropriate can be evaluated from the time evolution of the measured surface potential, as presented in Figure 4.12. In the first loading steps, the EMF curves reach a stable potential corresponding to MgH_2 formation within the 30 min waiting time, indicating that this time interval is sufficient to reach thermodynamic equilibrium. Stable potentials are also observed for hydride formation in the palladium capping layer. This is not true in the transition between the Mg hydride and the Pd hydride plateaus, where the EMF curves show a double plateau and an increased final slope (see Figure 4.12). A similar behavior has previously been observed by the author in Mg-Pd thin films loaded with high current densities, and related to hydrogen accumulation in the Pd capping layer due to the presence of a magnesium hydride blocking layer [92]. This interpretation is supported by the FEM diffusion simulations in section 4.4. The simulations show that, with a 350 nm closed layer of magnesium hydride, the waiting time of 30 min does not suffice to reach thermodynamic equilibrium. This is due to the low diffusivity of hydrogen in MgH_2 , even considering hydrogen transport through grain boundaries and a grain size of 100 nm. Therefore, after a closed MgH_2 layer is formed, the measured surface potential is mainly controlled

by hydrogen accumulation in the Pd capping layer. Considering the electrochemical isotherms in section 4.3, this implies that the surface potential of $\sim -800\text{mV}$ related to the $\text{Mg} \rightarrow \text{MgH}_2$ phase transition will only be observed until a closed hydride layer is formed. Therefore, the experimentally observed width of the MgH_2 potential plateau in electrochemical isotherms is directly related to the magnesium hydride blocking layer thickness. As will be presented in the rest of this section, the thickness of the blocking layer can give us information on the density of nucleation sites for the hydride phase, which are influenced by the loading conditions and by material properties.

Firstly, the effects of the loading parameters will be considered. For both Mg and ZK60, the plateau width of electrochemical isotherms increases, when decreasing the loading current density and maintaining a constant loading time (see Figure 4.16). As introduced in section 2.3.5, magnesium is known to form a hydride blocking layer due to the much slower diffusion of hydrogen in the hydride phase compared to the solid solution (see also section 2.3.6). It has moreover been shown that the thickness of the magnesium hydride blocking layer depends on the density of nucleation sites for the hydride phase [3, 4, 92, 112]. The density of nucleation sites, and therefore the thickness of the hydride blocking layer, can be influenced by the driving force to nucleation. The driving force to hydride nucleation depends on the supersaturation of the α -Mg matrix, which can be controlled through different parameters depending on the experimental technique, as described in section 2.3.5. In the case of electrochemical loading, the driving force to nucleation depends on the applied loading current and on the duration of the loading interval, which control the resulting hydrogen concentration according to Faraday's law (Eq. 2.25). In turn, the driving force to nucleation ΔG_V controls the critical radius r^* , which is the lowest radius for which a hydride precipitate is stable, according to [98]:

$$r^* = \frac{2\gamma}{\Delta G_V - \Delta G_S} \quad (5.1)$$

where γ describes the interface energy between Mg and MgH_2 , while ΔG_S describes the strain energy due to the volume difference between the two phases (see also section 2.3.5). Moreover, the driving force also influences the nucleation rate according to Eq. 2.13, where a higher driving force is related to a higher nucleation rate. Therefore, a high driving force will lead to fast nucleation of small hydride nuclei. In this situation, as suggested by Uchida et al. [3], the nuclei will quickly connect forming a closed hydride layer. Therefore, a higher driving force to nucleation is related to the formation of a thinner blocking layer.

In this work, the effect of the driving force to nucleation on the blocking layer is observed in the electrochemical isotherms of Mg and ZK60 samples obtained with different loading current densities, as presented in section 4.3.3. As expected from the model introduced in section 2.3.5, a lower driving force to nucleation – associated to a lower hydride nucleation rate and to larger

stable hydride nuclei – is related to a thicker blocking layer, because it takes longer until the growing hydride nuclei connect to form a continuous layer. This can be observed as a larger plateau in the isotherms in Figure 4.16. A larger plateau means that more hydrogen is absorbed in the sample during the Mg to MgH_2 phase transformation. Therefore, a larger fraction of magnesium is transformed in magnesium hydride before a closed blocking layer is formed. Once the blocking layer is formed, the equilibrium potential increases again, until the palladium hydride plateau is reached. These results highlight the importance of choosing adequate parameters for electrochemical hydrogen loading, which can strongly and directly affect the achieved hydride volume.

The effects of the different chemical compositions and microstructures on hydride formation can be discussed by comparing the electrochemical isotherms of Mg and ZK60 samples. From the isotherms in Figure 4.14, it appears that ZK60 samples in all deformation states have a smaller MgH_2 plateau compared to Mg samples.

To interpret this difference we have to consider the nucleation mode of magnesium hydride in these samples. The JMAK analysis in section 4.5.1 suggests heterogeneous nucleation for Mg and ZK60 at room temperature. In fact, both at room temperature and at 398.2 K, the measured Avrami exponents are close to $n = 1$. This might be interpreted as a linearly increasing density of nucleation sites, but with no spatial growth, according to Eq. 3.10 (see also Table 3.3). This interpretation is however not confirmed by the in-situ TEM results in section 4.7, where spatial growth of the hydride is observed. Therefore, the Avrami exponent can be more likely interpreted as 2-dimensional growth from a constant number of nucleation sites, limited by diffusion. A constant number of nucleation sites is usually associated with heterogeneous nucleation [189]. In the case of heterogeneous nucleation, the density of nucleation sites does not only depend on the driving force to nucleation, but it is also influenced by the presence of lattice defects and intermetallic phases [100, 146, 147]. As shown in sections 4.1.2 and 4.7, the ZK60 samples possess a large fraction of intermetallic phases dispersed over the whole sample surface and cross-section. These precipitates might act as nucleation sites for the hydride phase [146], increasing the nucleation rate and therefore leading to a faster formation of the hydride blocking layer, when present at the Mg-Pd interface. This explains the smaller plateau width in the ZK60 electrochemical isotherms compared to Mg. Therefore, the addition of Zr and Zn does not just reduce the grain size, but also affects the hydride formation.

The final aspect to consider is how HPT influences the electrochemical isotherms of magnesium and ZK60. For pure Mg, no effect on the hydride layer thickness is observed after severe plastic deformation. This suggests that, in this case, the grain size reduction to around 800 nm and the related introduction of lattice defects do not have a strong influence on the availability of nucleation sites for the hydride phase.

In the case of ZK60, on the contrary, an increase in the hydride blocking layer thickness is observed after HPT. Following the above logic, the availability of nucleation sites can affect the blocking layer thickness. For ZK60, the Zn and Zr rich precipitates are particularly relevant for hydride nucleation. While their overall spatial distribution is affected by HPT – especially in the cross-section as shown in section 4.1.2 – the surface distribution of intermetallic precipitates is not strongly affected by HPT (see Figure 4.3). Therefore, it does not seem likely that the wider plateau can be related to the modified distribution of intermetallic precipitates following HPT.

Another reason may be related to the kinetics of hydrogen diffusion and the defect densities of the samples, since the hydrogen diffusivity differs strongly for grains and grain boundaries. By decreasing the grain size from $\sim 10\ \mu\text{m}$ to $\sim 85\ \text{nm}$, the grain boundaries concentration increases from 0.04 % to 7.3 % (calculated assuming a 1 nm width of GBs) which provides a network of fast-diffusion pathways for hydrogen. This will promote hydrogen diffusion through the Mg hydride phase. Assuming that the grain boundaries do not form magnesium hydride, they could provide diffusion pathways for hydrogen, facilitating the diffusion from the Pd capping layer through the hydride layer, reaching the α -Mg volume which is yet to be transformed. As introduced at the beginning of this section, the 30 min waiting interval between subsequent loading steps is not sufficient to reach thermodynamic equilibrium once a closed layer of magnesium hydride is formed, as results both from experimental EMF curves (see Figure 4.12) and from the FEM diffusion simulation in section 4.4.

From the FEM simulation results, we can moreover estimate whether hydrogen diffusion in grain boundaries can affect the measured electrochemical isotherms. The diffusion simulations were performed assuming a diffusion coefficient of $D_H = 10^{-28}\ \text{m}^2/\text{s}$ for MgH_2 and $D_H = 10^{-16}\ \text{m}^2/\text{s}$ for grain boundaries in MgH_2 (see section 3.6.1). Experimental electrochemical isotherms are built by plotting the surface potential of palladium, which is measured against the reference electrode, as a function of hydrogen concentration in the sample. At thermodynamic equilibrium, the chemical potential of hydrogen is constant in the whole sample, and so the surface potential of palladium reflects the equilibrium potential for magnesium hydride formation. This ceases to be true once a closed blocking layer is formed, because hydrogen cannot diffuse quickly enough to achieve thermodynamic equilibrium in 30 min. However, the small amount of hydrogen diffusing at grain boundaries in HPT-ZK60 still decreases the global hydrogen concentration in palladium, and therefore affects the measured surface potential (see also section 2.3.3). The magnitude of this effect can be estimated through the FEM simulation results. Considering a mean grain diameter of 100 nm, after 30 minutes the amount of hydrogen that can diffuse from the Pd coating along grain boundaries in the 350 nm thick MgH_2 blocking layer is modest. The H concentration drops by $3 \cdot 10^{-4}\ \text{H/Pd}$ in the Pd capping layer, which would cause a variation of only $-1.6\ \text{mV}$ in the measured Pd potential (see Figure 4.18). Since the related surface potential variation caused by the H concentration increase in Pd from 0.009 H/Pd to 0.022 H/Pd would be of the

order of 30 mV, the -1.6 mV decrease caused by hydrogen diffusion into the Mg layer is too small to produce a noticeable difference in the measured electrochemical isotherms.

To summarize, the FEM simulations suggest that, due to the short waiting time between each loading step in comparison to the time scale of hydrogen diffusion through MgH_2 grains and grain boundaries, it is not likely to observe the effects of grain boundary diffusion by electrochemical loading. One might think of simply extending the waiting time after each loading step to allow for thermodynamic equilibrium even after the formation of the MgH_2 blocking layer. However, according to the FEM simulations, a waiting time of 30 h after each loading step would still not be sufficient to observe grain boundary effects with a grain size of 100 nm (see Figure 4.18). Considering the loading conditions described in section 3.4, a total of 150 loading steps are needed to achieve a hydride thickness of $1\text{ }\mu\text{m}$. Considering a waiting time of 30 h after each loading step, this would imply a total duration of more than 6 months to measure a single electrochemical isotherm, without considering that the time necessary to diffuse through the hydride layer will increase with the layer thickness. It is therefore not realistic to use electrochemical loading in order to observe grain boundary diffusion effects.

On top of this, the effects of the increased dislocation density resulting from HPT on ZK60 electrochemical isotherms have to be considered. As introduced in section 2.3.8, the stress field of hydrogen can interact with the stress field of dislocations in metals, resulting in an area with increased hydrogen concentration in the dilatation field below an edge dislocation line. This mechanism was studied in depth for Pd by Maxelon et al. [140]. Although this effect was not directly observed for Mg, the elastic energy for the interaction of hydrogen with dislocations can be calculated (see Figure 2.21), and is of the same order of magnitude as that of Pd, with a value of 5 GJ/mol at a distance of $1\text{ }\text{\AA}$ from the dislocation line in Mg and ZK60 against the 15 GJ/mol in the same position for Pd. For ZK60, Positron Annihilation Spectroscopy (PAS) results (section 4.6) prove an increase in the dislocation density as a consequence of HPT, compared to the as-extruded samples. As shown in section 4.6, the concentration of dislocations is below the PAS detection limit of about 10^{12} m^{-2} [213] for undeformed ZK60, and increases to values in the 10^{13} m^{-2} range after HPT. Considering the full thickness of HPT-ZK60 samples studied in this work, the change in the plateau width corresponds to a change of $c_H = 6.92 \times 10^{-5}\text{ H/Mg}$ in the hydrogen concentration. This increase in hydrogen capacity is observed in HPT-samples compared to undeformed ZK60 before the formation of a blocking layer (see Figure 4.14.b). Considering the hydrogen cylinder model (see section 2.3.8), which assumes a cylinder with increased hydrogen concentration to form below the dislocation line, we can use the sample's dislocation density to calculate how large the cylinder should be to accommodate this extra amount of hydrogen. According to the cylinder model [140] the hydrogen concentration at dislocations is given by:

$$c_{dist} = \delta \rho_d \pi R^2 \quad (5.2)$$

where R is the cylinder radius, ρ_d is the dislocation density, and δ is the fraction of interstitial sites occupied by hydrogen within the cylinder. Using as a representative value $\rho_d = 2.5 \times 10^{13} \text{ m}^{-2}$ and assuming an occupation of $\delta = 1$, the radius of the hydrogen cylinder should be $R \sim 9 \text{ \AA}$ to accommodate the extra hydrogen concentration of $c_H = 6.92 \times 10^{-5} \text{ H/Mg}$. The dislocation density chosen corresponds to half of the density at $r = 3 \text{ mm}$, close to the mid-radius for the HPT-samples. The total dislocation density was divided by 2 because hydrogen interacts more strongly with edge dislocations. The $9 \text{ \AA}$ hydrogen cylinder radius is close to the value for H in Pd measured by Maxelon et al. [140]. Comparing the elastic energy as a function of the cylinder radius in Figure 2.21, we would expect a smaller radius for magnesium compared to palladium. Nonetheless, the number is still reasonable if we consider that PAS tends to underestimate the dislocation density compared to other methods such as XRD, as explained in section 4.6.

Since the chemical potential related to hydrogen trapping at dislocations should be lower than the one for Mg hydride formation, the effect of dislocations should be seen as extending the solubility limit of hydrogen in hcp α -Mg, moving the onset of the two-phase region to higher hydrogen concentrations, assuming that equilibrium is achieved in the whole sample after each loading step. It is furthermore assumed here that the tensile stress field at the dislocation is filled within the Mg α -phase. However, for Mg it is difficult to judge these effects from electrochemical loading experiments. Considering the low solubility of hydrogen in Mg and the large size of the sample, the solubility limit is locally surpassed close to the Mg-Pd interface and the waiting time is not long enough to allow thermodynamic equilibrium in the whole depth of the sample (0.6 mm). Therefore, it is not surprising that only the potential related to magnesium hydride formation is observed, instead of that resulting from H trapping at dislocations. To measure the chemical potential related to H trapping at dislocations we would need to load with extremely low currents and time intervals, so that even the local concentration at the Mg-Pd interface does not surpass the solubility limit of H in Mg. In fact, only avoiding the formation of magnesium hydride we could measure experimentally the chemical potential related to hydrogen trapping at dislocations. Although this was not possible in this work, during the loading experiment hydrogen can diffuse in the magnesium α -phase surrounding the hydride nuclei, and interact with dislocations. This would not affect the measured potentials but it would lead, as observed, to a larger MgH_2 potential plateau.

Ultimately, it is not possible to prove by this measurement alone whether the slightly higher hydrogen capacity is caused by the increased dislocation density, but by combining the approaches of isotherm measurements, FEM simulations and PAS this hypothesis provides a reasonable explanation for the observed experimental results.

To conclude, electrochemical hydrogen loading is a suitable technique to observe the formation of the hydride blocking layer. As it was discussed, the thickness of the blocking layer depends both on the driving force to hydride nucleation, and on the density of sites for heterogeneous nucleation. In particular, for ZK60 we suggest that intermetallic precipitates can act as nucleation sites for the hydride phase. These results also indicate that, on the contrary, lattice defects such as grain boundaries and dislocations do not play an important role in MgH_2 nucleation, since we do not observe a variation in the hydride layer thickness when increasing their density by HPT. This goes in line with the assumption that grain boundaries in metal-hydrogen systems do not form hydride phases [137, 224].

However, electrochemical loading is not suitable for observing effects of hydrogen diffusion at grain boundaries in magnesium hydride, due to the long time scale of diffusion in MgH_2 and grain boundaries compared to the waiting time between electrochemical loading steps. Therefore, techniques allowing for longer diffusion times are necessary to let the effects of grain boundary diffusion emerge. In this work, this was achieved via gas-phase H loading, as discussed in the following section.

5.3 Microstructure effects during hydrogen absorption in Mg and ZK60 at room temperature

As discussed above, the 30 minutes timescale used in stepwise electrochemical loading is too short to observe the effects of grain-boundary diffusion. However, FEM simulations indicate that these effects become significant over longer timescales when the grain size is sufficiently small (see section 4.4). In particular, a significant transport through grain boundaries in the hydride layer is expected for grain sizes of $d = 100\text{ nm}$ and $d = 1\text{ }\mu\text{m}$. Therefore, to directly observe the effects of GB diffusion, experiments are required which allow hydrogen to diffuse for longer times. This was achieved by performing room temperature gas-phase loading in this work, where the sample is exposed to hydrogen in a chamber with a fixed volume and the experiment is only stopped when the hydrogen pressure reaches a constant final value, meaning that no more hydrogen is diffusing into the sample (see section 3.5).

In these conditions, enhanced hydrogen absorption is observed for pure Mg samples after HPT deformation, see chapter 4.5.1. Accounting for the different surface-to-volume ratios, a 20% increase in the hydride layer thickness is observed in the HPT-deformed samples (see Table 5.1). The Mg samples were loaded with the same starting hydrogen pressure $P_0 = 0.1\text{ mbar}$, and according to the electrochemical isotherms (see Table 4.2), they have the same equilibrium pressure of $\sim 4\text{ }\mu\text{bar}$ for hydride formation at room temperature. Therefore, the applied overpotential is similar for all samples, and hence the driving force to hydride formation is expected to be the

same for both deformation states. Moreover, the electrochemical loading experiments showed a similar width of the hydride layer, which is related to a similar density of hydride nucleation sites. As the nucleation of hydrides happens at the interface between the Pd and the Mg, it can be assumed that the density of hydride nucleation sites is the same for both types of measurements. On top of this, the electrochemical loading results suggest that the grain boundaries do not act as hydride nucleation centers (see section 5.2). Combining these premises reveals that the observed improvement in hydrogen absorption during gas phase loading can be attributed to the effect of grain boundaries, promoting hydrogen diffusion in the hydride layer. An even larger effect is observed for ZK60, where the amount of absorbed hydrogen increases by 65% after HPT (see Table 5.1). Also here, the increase is attributed to the hydrogen diffusion at grain boundaries, and not on hydride nucleation at grain boundaries.

Based on the data given in Table 5.1, hydrogen gas absorption at room temperature can be compared across the different chemical compositions and deformation states. While undeformed ZK60 still absorbs less hydrogen compared to undeformed magnesium during gas loading, the difference is less severe than for electrochemical loading, confirming that the longer waiting time decreases the influence of the nucleation site density on the total amount of absorbed hydrogen. Interestingly, the total amount of absorbed hydrogen is similar for HPT-deformed ZK60 and Mg. A larger difference may be expected considering only the average grain size, which is ~ 790 nm for HPT-Mg and ~ 85 nm for HPT-ZK60. However, according to the low-temperature dynamic recrystallization mechanism (LTDRX) introduced in section 2.1.1, HPT-Mg might also have an excess of dislocations in the vicinity of grain boundaries and dislocation pile-ups in the interior of the recrystallized grains, which can also promote hydrogen diffusion. Moreover, next to microstructural defects ZK60 has a high concentration of intermetallics that promote hydride precipitation and lead to a quicker formation of the blocking layer, as visible both during electrochemical loading and by comparing room temperature gas loading of undeformed Mg and ZK60.

Hydride formation at room temperature (298 K) was also examined via in situ TEM hydrogen loading at 6.67 mbar on Pd-coated HPT-ZK60. The pressure used for in-situ gas loading is above the equilibrium pressure for hydride formation in Mg at room temperature. The overpressure is

Table 5.1: Equivalent thickness of the magnesium hydride layer formed during room temperature hydrogen gas loading (see section 4.5.1). The increase of the equivalent hydride thickness is reported for HPT samples in comparison to as-extruded samples in the last column.

	Equivalent MgH_2 thickness		Change by HPT
	as-extruded	HPT	
Mg	(389 ± 2) nm	(465 ± 1) nm	+ 20%
ZK60	(285.7 ± 0.8) nm	(471 ± 2) nm	+ 65%

high compared to bulk gas-loading experiments, and its choice was fixed as the lowest value applicable in the atmosphere holder. As revealed by EELS in Figure 4.31, a hydride layer of approximately 200 nm forms after 12 h of loading, initiating at the Mg-Pd interface. The experiment was stopped after 12 h, but further hydrogen absorption under the same conditions may be observed over longer time scales. The absorption rate leading to the formation of 200 nm in 12 h in the TEM lamella is much shorter than that for hydrogen absorption in bulk HPT-ZK60, where the first hydrogenation step lasts nearly 200 h, leading to an equivalent hydride layer thickness of ~ 45 nm (see Table 4.3). The value is closer to that of undeformed ZK60, which completes its first absorption step within 24 h with an equivalent hydride thickness of ~ 70 nm (see Table 4.3). A similar effect is observed for pure magnesium samples too, where the first absorption is completed within 12 h for undeformed samples reaching a thickness of ~ 80 nm, and within more than 60 h for HPT-samples reaching a thickness of ~ 70 nm in ex-situ gas loading experiments. Since this discrepancy is not observed by in-situ TEM hydrogenation, it might be related to damages of the Pd capping layer occurring during HPT. In fact, the samples are coated with Pd before HPT deformation, to avoid altering the Mg or ZK60 microstructure during sputter coating, which increases the temperature of the sample. However, during HPT the Pd layer is compressed and sheared with a pressure of 5 GPa between the machine anvils. Although, as visible in the TEM (see Figure 4.30), the Pd layer is still intact after HPT, the surface can be contaminated with material transferring from the anvils, which can later prevent hydrogen absorption. Local detachment of the Pd coating is also likely to happen. TEM lamellas avoid the problem of contaminated Pd surfaces, because the lamella preparation creates a clean palladium surface in the coating layer (perpendicular to the Mg-Pd interface) which was not in contact with the HPT anvils.

To summarize, the hydrogen absorption kinetics appeared much slower in both Mg and ZK60 samples after HPT in ex-situ hydrogen loading at room temperature. This behavior was not confirmed by in-situ TEM loading, where the kinetics of HPT-ZK60 is much faster than for ex-situ loading, and more similar to that of undeformed ZK60. These differences cannot be related to driving force effects since all samples were loaded with the same hydrogen overpressure and have a similar equilibrium pressure according to the electrochemical loading results (see section 4.3.2). These differences can be attributed to contamination of the Pd capping layer during HPT, which is not relevant for in-situ TEM since a new clean surface is created during the lamella preparation. These lamella sides are suggested to offer hydrogen entry paths through the Pd layer into the Mg or ZK60, respectively.

The effect of contamination of the Pd surface during HPT can also be discussed for in-situ and ex-situ hydrogen loading at 398.2 K. No difference in kinetics between as-extruded and HPT-deformed samples was observed for bulk samples loaded at 398.2 K, which further suggests that the reason for sluggish kinetics in HPT samples at room temperature is not related to the material

itself, but to the HPT effect on the capping layer. The partial inactivity of the capping layer in the dissociation and absorption of hydrogen due to contamination can be mitigated by hydrogen diffusing and redistributing within the Pd layer, and by the higher splitting rate of H_2 molecules at a higher temperature.

To estimate this effect, we can consider literature values for hydrogen diffusion in palladium which are about $D_H = 3 \cdot 10^{-11} \text{ m}^2/\text{s}$ at room temperature and $D_H = 2 \cdot 10^{-10} \text{ m}^2/\text{s}$ at 398.2 K [225]. With those diffusion coefficients, the times necessary for hydrogen to diffuse for 1 mm in Pd are about 8 h at room temperature, and about 1 h at 398.2 K. Therefore, we expect a higher impact of hydrogen redistribution in the Pd capping layer in the results for loading at higher temperatures. This further suggests that the slower hydrogen kinetics in HPT-deformed Mg and ZK60 at room temperature may be related to a contamination of the Pd capping layer during HPT.

Beyond these global considerations of hydrogen absorption and hydride formation at room temperature and higher temperatures, a further observation from the in situ TEM loading reveals that, in one region of the sample, the hydride layer penetrates deeper than elsewhere in the lamella, reaching nearly 500 nm compared to the 200 nm observed in the rest of the sample. To assess whether this different hydride growth is related to the local microstructure, the hydrided region was overlaid with a HAADF bright-field image of the unloaded sample, as shown in Figure 5.1. Due to the bright-field imaging mode, intermetallic precipitates appear as dark spots, unlike in the HAADF and SEM images presented in Sections 4.7 and 4.1.2. As seen in Figure 5.1.a, the distribution of intermetallics varies in concentration across the lamella. Apparently, the area where the hydride layer extends more deeply lies within a region of elevated intermetallic particle content near the Mg–Pd interface. While heterogeneous hydride nucleation in ZK60 has already been related to intermetallic second phase precipitates as nucleation centers, there are further reasons why a higher density of Zn-rich particles may facilitate hydride formation. As introduced in Section 2.1.1, precipitates influence the plastic deformation of magnesium alloys by stabilizing low-angle grain boundaries and preventing dislocation annihilation. Consequently, grain refinement may be more pronounced in regions with higher intermetallic content, leading to an increased density of grain boundaries and dislocations. In turn, this can promote hydrogen diffusion and hydride nucleation.

To conclude, complex effects that determine hydrogen diffusion and hydride formation during gas loading of as-extruded and HPT-deformed samples at room temperature emerge. Unlike for electrochemical loading, where effects related to hydride nucleation are mostly visible, gas loading allows to also observe diffusion effects thanks to the longer waiting times. As seen in FEM simulations (see section 4.4), for sufficiently small grain sizes, effects related to grain boundary diffusion can be expected at long times. For both Mg and ZK60, the hydrogen capacity increases after HPT deformation. Thereby, the total amount of absorbed hydrogen depends on the

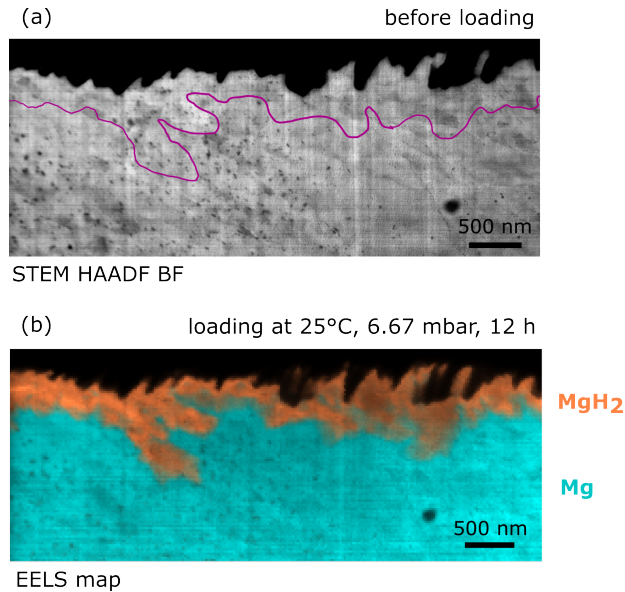


Figure 5.1: (a) STEM HAADF BF image of the HPT-ZK60 sample before hydrogenation. The purple overlay shows the area which was later transformed into magnesium hydride. (b) EELS map for hcp Mg and Mg hydride after 12 hours of loading at room temperature. The area where the hydride reaches the largest depth has a large concentration of second-phase precipitates before hydrogenation.

interplay between the formation of a blocking layer and the diffusion through the blocking layer via grain boundaries. For ZK60 samples, intermetallic precipitates lead to a finer microstructure which promotes hydrogen diffusion, but they can also act as nucleation sites for the hydride phase, leading to a faster formation of the hydride blocking layer.

After HPT, the total achieved hydride thickness increases from ~ 286 nm to ~ 470 nm in ZK60, and from ~ 390 nm to ~ 465 nm in Mg. This shows that increasing the grain boundaries concentration can improve the hydrogen capacity of Mg and ZK60 samples, leading to larger hydride volumes. In this work, no improvement of hydride formation kinetics was observed during bulk gas-phase loading at room temperature. This effect is attributed to degradation of the Pd capping layer after HPT.

5.4 Microstructure effects and evolution during hydrogen absorption in ZK60 at 398.2 K

The previous sections showed how microstructure affects hydrogen absorption in Mg and ZK60 at room temperature. In particular, for gas-phase hydrogen loading at room temperature, the

hydrogen capacity of ZK60 increases after HPT, with the thickness of the hydride layer going from ~ 286 nm to ~ 470 nm. In ex-situ loading experiments the absorption kinetics was slower for HPT-ZK60 compared to undeformed ZK60. This effect was however not observed by in-situ TEM hydrogen loading, and was attributed to surface contamination of the Pd capping layer resulting from HPT deformation. Further gas-loading experiments were performed at 398.2 K, to study if the microstructure effects measured at room temperature persist at higher temperatures. Moreover, cyclic loading and unloading was performed to observe how the hydrogen capacity changes beyond the first hydrogenation.

Hydrogen absorption and desorption of ZK60 samples in different deformation states has been studied at a temperature of 398.2 K, by exposing the samples to a hydrogen gas pressure of ~ 20 mbar. According to the van't Hoff plot for the Mg to MgH_2 phase transformation (see Figure 2.16), this pressure exceeds the equilibrium pressure of 2 mbar for hydride formation at 398.2 K and should therefore provide sufficient driving force for hydride nucleation. Loading experiments have been performed both on bulk samples (section 4.5.2) and on TEM lamellas (section 4.7); here, these results are further discussed and compared.

As shown in Figure 4.24, ZK60 bulk discs were loaded and unloaded for 5 times consecutively in both the as-extruded and HPT-deformed state. The first absorption will firstly be discussed. For undeformed ZK60, an equivalent hydride layer thickness of ~ 1.4 μm is reached after about 4 hours. Similarly, for HPT-ZK60 an equivalent thickness of ~ 1.5 μm is reached after around 4.5 hours. Since the two values overlap within their error bars (see Table 4.4), no relevant difference in the hydrogen capacity of the two samples arises. However, the recorded absorption curves show different shapes (see Figure 4.24). While for HPT-ZK60 the gas pressure starts dropping immediately, and gradually slows down after about 2 h, an initial delay with a slower pressure drop is observed for undeformed ZK60. Interestingly, this initial slower absorption is observed also for HPT-ZK60 in later loading cycles. This behavior is sometimes described as an incubation period and is often attributed to nucleation of the hydride phase and to the cracking of the magnesium oxide layer [6, 157, 159, 226]. Since, however, in this work the samples are coated with palladium, the oxide layer hypothesis can be discarded. The faster nucleation of the hydride phase in the first loading of HPT deformed ZK60 can be explained by the characteristic (0002) texture of the HPT-ZK60 sample, that results from the HPT process, as presented in section 2.3.9. This texture constitutes a favorable direction for the formation of MgH_2 and was associated to faster absorption kinetics compared to other orientation relationships between Mg and MgH_2 [159, 161] (see also section 2.3.9). This process is represented schematically in Figure 5.2. After the decomposition of the hydride layer during the unloading step, the original HPT texture is lost [161], explaining the appearance of an incubation period for the following loading cycles of HPT-ZK60, that resembles the behaviour of the as-extruded ZK60 with its random grain structure. The second hydrogenation is represented schematically in Figure 5.3.

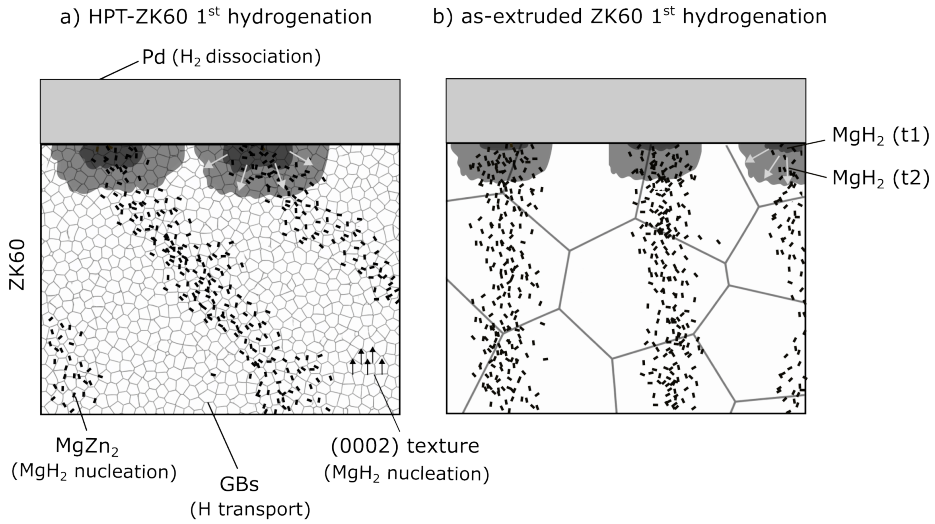


Figure 5.2: Schematic representation of the first hydrogenation cycle in HPT-deformed and as-extruded ZK60 at 398.2 K. The main aspects affecting hydrogen kinetics are represented, namely hydrogen molecule dissociation on the Pd surface, hydrogen transport at grain boundaries and the effect of texture and intermetallic precipitates on hydride nucleation and growth. The intermetallic precipitates are represented as black dots and they form bands similarly to what observed in section 4.1.2. The hydride evolution is represented at two subsequent times t_1 and t_2 . At t_1 , a larger volume is hydrided in HPT-ZK60 compared to as-extruded ZK60 because the (0002) texture eliminates the incubation time.

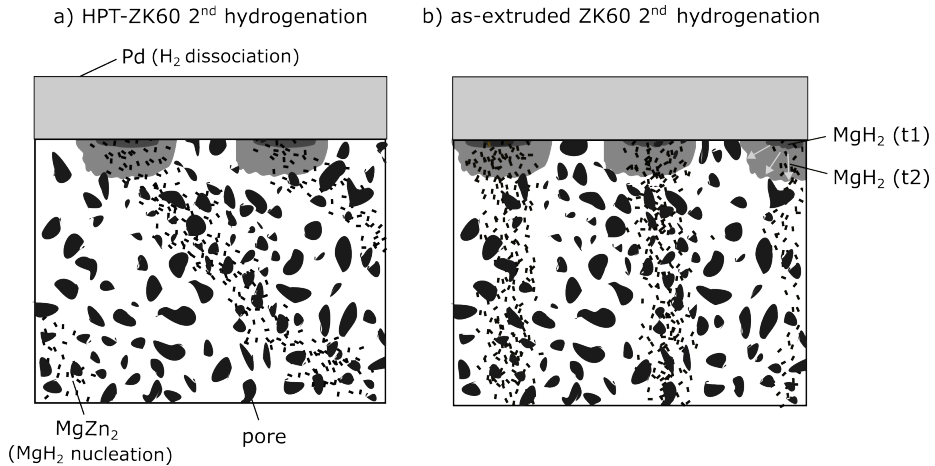


Figure 5.3: Schematic representation of the second hydrogenation cycle for HPT-deformed and as-extruded ZK60. The microstructure in the alpha-phase is now porous for both samples, and no (0002) texture is present. The pores are not visible in the MgH_2 area due to the volume expansion during hydride formation. The intermetallic precipitates are represented as black dots and they form bands similarly to what observed in section 4.1.2. The hydride evolution is represented at two subsequent times t_1 and t_2 , and is similar for both samples.

The first hydrogenation results can be compared to the in-situ TEM loading results at the same temperature and pressure (Figure 4.33). This experiment was performed on the same lamella used for in-situ TEM at room temperature, after removing the hydride phase by heating. Here, a hydride layer of $\sim 1.5 \mu\text{m}$ thickness is observed after 2 hours, which is sufficiently close to the bulk value of $1.5 \mu\text{m}$ MgH_2 achieved in ~ 4.5 h during the first loading of HPT-ZK60 (see Table 4.4).

Moreover, a slower initial kinetics is revealed also by in-situ TEM. As can be observed in Figure 4.33.b, after 50 min only a small portion of the lamella is hydrided, extending to a depth of ~ 500 nm. This is close to the incubation period of ZK60 (both HPT and undeformed), which lasts about 1 h (see Figure 4.24). Since during in-situ TEM loading hydrogen enters from a clean surface in the Pd capping layer which is created perpendicularly to the Mg-Pd interface during the lamella preparation, we can further exclude that the incubation period is caused by dissociation problems at the sample surface. Although the TEM sample was treated by HPT, the absence of the incubation period observed for the first loading of bulk HPT-ZK60 is not to be expected, since the TEM sample had previously been loaded at room temperature. This result confirms the previous interpretation of bulk hydrogen absorption curves that the incubation time is related to hydride precipitation and can be controlled by the orientation of Mg.

The next aspect to consider is the apparent loss of capacity of the ZK60 samples after the first loading cycle, that was shown in chapter 4.5.2. This can also be related to the in-situ TEM experiments on HPT and as-extruded ZK60 samples. As shown in section 4.5.2, both HPT-deformed and as-extruded ZK60 bulk samples show a loss of capacity close to 30% after the first loading cycle. Afterwards, the amount of absorbed hydrogen remains constant in cycles 2 to 5.

This can be explained by the porous microstructure observed by in-situ TEM. As shown in section 4.7, pores of sizes between 50 nm and 100 nm are formed after the first hydrogen desorption, independently of the loading and unloading conditions. The formation of the pores might be caused by the 30% volume contraction related to the $\text{MgH}_2 \rightarrow \text{Mg}$ phase transformation during unloading (see section 2.3.2). In this case, after the first dehydrogenation, we expect a reduction of about 30% in the density of the uppermost magnesium layer. We also expect that the hydride layer thickness, which is limited by diffusion, is constant for all loading cycles. With these assumptions, during the second absorption, the volume which is transformed to MgH_2 will contain 70% Mg and 30% empty volume due to pores. Therefore, the total moles of magnesium which can be transformed to MgH_2 decreases by 30% compared to the first absorption, and so does the total amount of absorbed hydrogen. This behavior is observed experimentally during cyclic loading of ZK60 in Table 4.4, with no dependence on the deformation state.

As shown in Figure 4.32, with subsequent hydrogenation the Mg layer expands again and the pores are no longer visible. This allows to reach again a hydride layer of a similar size during the

following loading steps. Interestingly, this means that the existing pores suffice to accommodate for the local volume expansion associated with hydride formation.

The microstructure evolution of bulk magnesium with hydrogenation and dehydrogenation cycles, as presented in chapter 4.7, has rarely been studied in the literature. Usually, hydrogen absorption is studied for magnesium powders or for thin films, where the absorption is faster due to the shorter diffusion lengths and the enhanced surface-to-volume ratio. The resulting microstructure of powders after hydrogen desorption is often considered in Hydrogen Disproportionation Desorption Recombination (HDDR) studies. The HDDR technique is used to refine the microstructure of metal samples through absorption and desorption of hydrogen, leading to grains in the 20 - 100 nm range for Mg-Al-Zn and Mg-Zn-Zr alloys [207, 227–231]. For thin films, a nanocrystalline structure is also observed after hydride decomposition [115]. For magnesium powders the particle size is similarly reduced by hydrogenation and dehydrogenation cycles [9, 12, 228]. In all cases this effect can be attributed to the volume variations happening during the formation and the decomposition of the hydride phase. On top of this, in the case of bulk magnesium, a porous structure has been reported following dehydrogenation by Guo et al. [232]. Pore formation can be the first step in powderization, which is often observed in cyclic hydrogenation and dehydrogenation of magnesium-based chips obtained by filing [9]. This suggests that the mechanism observed in this work is not limited to bulk magnesium, but could also affect magnesium chips in the μm range.

The porous microstructure obtained for bulk Mg samples might seem advantageous for further hydrogenation. In fact, if hydrogen was penetrating at high pressures within the pores, the large non-oxidized surface and low diffusion distances would provide favorable conditions for fast hydrogenation. In reality, for this type of sample the newly formed pores are not in contact with the loading hydrogen gas because the Pd coating layer is still intact after dehydrogenation. Therefore, any hydrogen gas present in the pores must be in equilibrium with the surrounding magnesium and magnesium hydride matrix. Its pressure will therefore not exceed the equilibrium pressure for Mg hydride formation at 398.2 K, which is around 2 mbar (see Figure 2.16). Considering the total volume of the pores in the hydrided depth of $1.5\ \mu\text{m}$ and a pressure of 2 mbar, a total of $\sim 2 \times 10^{-12}$ mol of H_2 gas would be present in the pores at equilibrium, which is negligible compared to the total amount of absorbed hydrogen $n_{abs} \sim 10^{-5}$ mol (see Table 4.4). This also means that eventual hydrogen gas inside the pores will not contribute to the propagation of the hydride front, as it lacks the overpressure to drive the dissociation of the H_2 molecules and the nucleation of the hydride phase. Nonetheless, similar structures can have the potential to promote faster hydrogen absorption by creating a direct contact between the loading hydrogen gas and the pores surface.

To conclude, hydrogen absorption and desorption studies at 398.2 K were performed both on bulk samples and by in-situ TEM loading. The microstructure effect observed at room temperature,

where the hydride volume increased after HPT (as discussed in section 5.3), is no longer revealed at 398.2 K. This can be explained by the thermal instability of the lattice defects introduced by HPT, as introduced in section 2.3.9. Nonetheless, the thickness of the achieved hydride layer and the time necessary for hydrogenation are close to what is observed in SPD magnesium samples at similar and higher temperatures. For example, hydride formation is observed in Mg chips whose thickness is in the μm range in less than 1 h at temperatures close to 573 K [5]. As introduced in section 2.3.9, usually hydrogen absorption studies in Mg are performed on filings or powders obtained from bulk materials without any coating. This can cause secondary effects of the microstructure on hydrogen kinetics, because materials with increased hardness after SPD produce finer chips with a higher surface-to-volume ratio after filing, which in turn improves the kinetics of hydrogen absorption [151]. Thus, it is hard to differentiate direct microstructure effects due to transport at grain boundaries from indirect effects driven by a more favorable surface morphology.

Because of the large barrier to dissociation of hydrogen molecules on magnesium surfaces (see section 2.3.1), it is hypothesized that dissociation may be the rate-limiting step during magnesium hydride formation [75]. Moreover, as introduced in section 2.3.1, dissociation of H_2 on magnesium oxide has an even higher potential barrier than dissociation on clean Mg. Therefore, the surface morphology and the eventual oxidation of the studied magnesium samples cannot be disregarded when interpreting hydrogen absorption kinetics.

In this work, magnesium samples were coated with palladium, where H_2 dissociation happens without a potential barrier (see section 2.3.1). Therefore, we don't expect H_2 dissociation to be the rate-limiting step to hydrogen absorption at 398.2 K. In this situation, no large difference in hydrogenation and dehydrogenation kinetics emerges between undeformed and HPT-deformed ZK60 (both ex- and in-situ). Therefore, the results of this work suggest that the improved hydrogenation kinetics after SPD reported in literature at temperatures close to 600 K (see section 2.3.9) may be primarily related to surface effects, rather than to hydrogen transport at grain boundaries.

6 Summary and Outlook

The central motivation of this work was to clarify how severe plastic deformation (SPD)-induced microstructures, especially grain boundaries, control hydrogen absorption and hydride formation in Mg and Mg-alloys. In particular, the Mg-Zn-Zr alloy ZK60 was studied in comparison to pure Mg. This alloy was chosen because of the small grain size achievable by severe plastic deformation. The samples' microstructure was altered by high-pressure torsion (HPT), and characterized by electron microscopy and positron annihilation spectroscopy (PAS). Hydrogen absorption was studied at two temperatures (room temperature and 398.2 K) using the two complementary methods of electrochemical and gas-phase loading, to address different aspects of thermodynamics and kinetics of the hydrogen-metal interactions. The experiments were combined with FEM diffusion simulations. For ZK60, gas loading of bulk samples was also compared with in situ TEM hydrogen loading, performed in hydrogenation and dehydrogenation cycles.

Regarding the samples' microstructure, ZK60 shows in all deformation states a complex distribution of intermetallic precipitates containing Zn and Zr, whose distribution changes as a consequence of HPT. In detail, intermetallic precipitates are distributed in bands parallel to the extrusion direction in as-extruded ZK60. The intermetallics are due to dynamic precipitation during extrusion, and their distribution in bands may be related to initial chemical inhomogeneities in the cast material. After HPT, the vertical bands are broken in shorter lines with varying orientations, depending on the position across the disc's radius. Both for ZK60 and Mg, HPT strongly diminishes the grain size. The average grain size goes from the millimeter range for undeformed Mg to 790 nm with a variance of 220 nm² for HPT-Mg. No variation in the grain size is observed for Mg samples deformed and characterized at temperatures below 223 K, in comparison to samples processed at room temperature. The initial grain size of ZK60 is 7 μ m with a variance of 16 μ m², which drops to 85 nm with a variance of 0.5 nm². This grain size was in the targeted range. For HPT-ZK60, an increased dislocation density ρ_d is measured after HPT by PAS, with values in the 10¹³ m⁻² range increasing along the disc's radius, while the dislocation density of undeformed ZK60 is below the detection limit of PAS, meaning below 10¹² m⁻² [213]. In total, the obtained microstructures were attributed to the low temperature dynamic recrystallization (LTDRX) processes happening during HPT due to the large introduced shear strain, as proposed for plastic deformation of Mg-based materials.

Hydrogen absorption was studied at room temperature using both electrochemical and gas-phase loading. To allow for hydrogen absorption, the samples were coated with a layer of Pd by ion beam sputtering, after removing the magnesium oxide layer in ultra-high vacuum conditions. Electrochemical loading mostly reveals effects related to hydride nucleation, since it is not possible to extend the waiting interval between loading steps long enough to accommodate hydrogen diffusion in magnesium hydride and at grain boundaries. It is known that magnesium forms a hydride blocking layer close to the surface. This slows down the absorption of hydrogen because of its low diffusivity in the hydride phase compared to α -Mg. After a closed blocking layer of magnesium hydride is formed, the measured surface potential is controlled by hydrogen accumulation in the Pd capping layer. Therefore, the MgH_2 plateau width measured in electrochemical isotherms was interpreted to correspond to the hydride blocking layer thickness. This interpretation is supported by FEM simulations for hydrogen diffusion through magnesium hydride with different grain sizes, showing negligible diffusion of hydrogen in the first 30 min, and by the time evolution of the surface potential curves, showing a shape characteristic of hydrogen accumulation in the Pd capping layer. In detail, the thickness of the forming blocking layer is strongly influenced by the applied overpotential and by the availability of nucleation sites. This is visible when comparing curves with different loading current densities, where the hydride layer thickness increases by more than a factor of two when decreasing the current density from $80 \mu\text{A}/\text{cm}^2$ to $20 \mu\text{A}/\text{cm}^2$. Moreover, we propose that the intermetallic precipitates in ZK60 may act as nucleation sites for the hydride phase. This leads to a reduced equivalent hydride layer thickness of $\sim 100 \text{ nm}$, compared to the $\sim 200 \text{ nm}$ of magnesium under the same conditions. No large difference is observed in the hydride layer thickness following HPT, apart from a $\sim 20 \text{ nm}$ increase for HPT-ZK60, which may be related to hydrogen interaction with dislocations. This indicates that the defects introduced by HPT do not act as nucleation sites for the hydride phase.

Effects related to hydrogen diffusion at grain boundaries were studied by hydrogen gas loading, where long waiting times can be realized. According to the FEM diffusion simulations, relevant transport through the hydride layer via grain boundaries can be expected for grain sizes below $1 \mu\text{m}$, and should therefore be relevant for HPT-deformed ZK60 and Mg. At room temperature, in fact, both materials show an increased hydrogen capacity, resulting in an equivalent hydride layer thickness of $(389 \pm 2) \text{ nm}$ for undeformed Mg and of $(465 \pm 1) \text{ nm}$ for HPT-Mg (+20%). The equivalent hydride layer thickness is $(285.7 \pm 0.8) \text{ nm}$ for undeformed ZK60 and $(471 \pm 2) \text{ nm}$ for HPT-ZK60 (+65%).

Despite the much smaller grain size, HPT-ZK60 does not absorb significantly more hydrogen than HPT-Mg, highlighting the opposing action of intermetallic precipitates: on the one hand, they enable the formation of a finer microstructure which promotes hydrogen diffusion. On the other hand, they lead to a faster formation of the hydride blocking layer due to enhanced hydride nucleation at the intermetallic precipitates.

Loading at room temperature was also studied by in-situ TEM and EELS mapping for HPT-ZK60. It appears that a 200 nm hydride layer forms in 12 h, which is compatible with the loading times for undeformed samples but shorter than the times for HPT samples. In fact, for bulk gas-phase loading of HPT-ZK60 and HPT-Mg a slower hydrogen absorption kinetics was observed, compared to the undeformed samples. This slower kinetics could be attributed to surface effects resulting from damages to the Pd capping layer during HPT. This issue is not present during in-situ TEM because an uncontaminated Pd surface is created during the TEM lamella preparation.

In-situ TEM hydrogen loading at different temperatures and pressures reveals the formation of pores with sizes in the 50 nm-100 nm range following the 30% volume reduction of the metal during hydride decomposition. When loaded again with hydrogen, the pores are no longer visible following the volume expansion of hydride formation, allowing reversible hydrogenation and dehydrogenation. The whole sample, including the Pd capping layer, remains intact after pore formation, at least in the first five cycles studied in this thesis. The porous structure decreases the density of magnesium in the hydrided and dehydrided depth, causing an apparent reduction in the calculated hydrogen capacity based on a similar diffusion length for the same diffusion time. These effects are observed for bulk as-extruded and HPT-deformed ZK60 samples that were loaded for 5 cycles at 398.2 K with a pressure of $p_{H_2} = 20$ mbar, and unloaded at the same temperature with a pressure lower than 10^{-4} mbar. For bulk samples, the equivalent thickness of the hydride layer is $(1.43 \pm 0.04) \mu\text{m}$ for undeformed ZK60 and $(1.50 \pm 0.04) \mu\text{m}$ for HPT-ZK60, which are achieved in about 4 h. This behavior agrees with in-situ TEM results, where under the same conditions the formation of a hydride layer of about $1.5 \mu\text{m}$ was observed within 2 h.

During gas-phase loading at 398.2 K, effects of texture appear during cyclic hydrogenation of HPT-ZK60. During the first hydrogenation of HPT-ZK60, no incubation time is observed, while subsequent cycles show an incubation time close to 40 min. A similar incubation time is observed also during the hydrogenation of as-extruded ZK60. This effect is attributed to the (0002) orientation achieved after HPT deformation, which provides a favorable orientation for MgH_2 precipitation and was associated with improved hydrogenation kinetics [159, 161].

At 398.2 K, no changes in the thickness of the hydride layer and in the absorption and desorption times appear in ZK60 after HPT deformation. Therefore, unlike at room temperature, no strong effect of grain-boundary diffusion on hydrogen absorption is observed. This may be related to the thermal instability of defects introduced by high-pressure torsion, such as grain boundaries, vacancies and dislocations [146], and to the fact that H diffusion in the hydride phase increases with temperature, enabling the formation of a thicker hydride layer. Nonetheless, the achieved results of hydriding a $1.5 \mu\text{m}$ depth in 4 h are relatively good. Usually, as a result of severe plastic deformation hydride formation is observed in Mg chips (whose thickness is in the μm range) in less than 1 h at much higher temperatures close to 600 K. The results of this work suggest that

these kinetic improvements reported in literature for Mg-based alloys deformed by SPD may be largely related to the more favorable surface morphology of the obtained chips, rather than to hydrogen transport at grain boundaries, especially for the initial loading cycles.

Therefore, in future studies the focus should be shifted from refining the microstructure of magnesium-based storage materials to improving the properties of the magnesium surface, by preventing its oxidation and by creating structures with a large surface area and short diffusion lengths. A porous structure similar to the one obtained from the dehydrogenation of bulk samples may serve this purpose by providing a large surface-to-volume ratio if the hydrogen gas can penetrate within the formed pores and dissociate on the pores' surface to be absorbed in the metal. Assuming that the samples are not exposed to air during the loading-unloading cycles the newly formed magnesium surfaces in the pores should be free of magnesium oxide and therefore favor the dissociation of H_2 molecules. Otherwise, also films with a thickness in the μm range would be advantageous as they may be more easily coated with catalytic materials compared to spherical powder particles or filings, and they could be completely hydrogenated already at 400 K. While their role may be secondary at higher temperatures, the effects of grain-boundary diffusion should not be disregarded for room temperature applications, especially over long time scales. Moreover, defects introduced by severe plastic deformation can become relevant in maintaining the hydrogen capacity during long-term cycling [146, 147], meaning that this technique can still have a positive effect on hydrogen kinetics in a different context from what was studied in this work.

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A Relation between absorbed gas and pressure drop with variable system temperature

In this appendix, the relation between the absorbed moles of H_2 gas, n_{abs} , and the recorded pressure variation ΔP in a system containing two different volumes V_1 and V_2 at different temperatures T_1 and T_2 is derived. The result is Equation 3.8, which can be used to relate the hydrogen absorption to the measured pressure drop during hydrogen loading at 125 °C.

Figure A.1 represent the model used to derive the equation. The initial condition is a system of two different volumes V_1 and V_2 at different temperatures T_1 and T_2 , with a constant pressure P_{in} throughout the system. A sample in V_1 is capable of absorbing gas molecules. Similarly to the experimental conditions, the systems is closed, so that the global number of gas molecules in the two volumes and in the sample remains constant. In order to have a constant pressure in the system, the two volumes at different temperatures will also have different densities $\rho = n/V$ of the gas molecules. If we assume that the gas follows the ideal gas low, a constant pressure is achieved when:

$$\rho_1 T_1 = \rho_2 T_2 \quad (A.1)$$

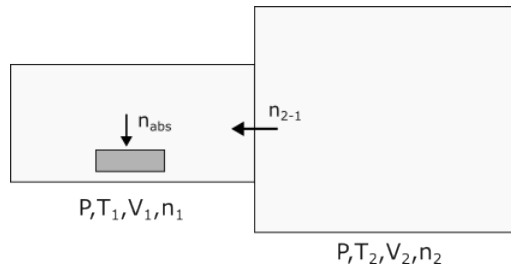


Figure A.1: Schematic model for the derivation of Equation 3.8. A system consists of two different volumes V_1 and V_2 at different temperatures T_1 and T_2 . The pressure is constant throughout the system. A certain amount of gas n_{abs} is absorbed in V_1 , to maintain a uniform pressure in the whole system, a certain number of gas molecules n_{2-1} has to move from V_2 to V_1 .

Now we consider that a certain amount of gas molecules n_{abs} is absorbed by the sample in V_1 , altering the density ρ_1 . To maintain a uniform pressure in the system, according to Equation A.1, the density ρ_2 has to change accordingly. Since the system is closed, a change of density in V_2 can only be achieved by the diffusion of gas molecules towards V_1 ; the number of these diffusing molecules is described as n_{2-1} .

Considering $n_{1,in}$ and $n_{2,in}$ the initial moles of gas in the two volumes, and applying the boundary condition of a closed system, we get that after absorption:

$$n_{1,fin} = n_{1,in} - n_{abs} + n_{2-1} \quad (\text{A.2})$$

$$n_{2,fin} = n_{2,in} - n_{2-1} \quad (\text{A.3})$$

Applying the condition in equation A.1 in the final state, we have:

$$\frac{T_2}{V_2}(n_{2,in} - n_{2-1}) = \frac{T_1}{V_1}(n_{1,in} - n_{abs} + n_{2-1}) \quad (\text{A.4})$$

From which we can express n_{2-1} as:

$$\begin{aligned} n_{2-1} &= \frac{T_2/V_2 \cdot n_{2,in} - T_1/V_1 \cdot (n_{1,in} - n_{abs})}{T_1/V_1 + T_2/V_2} = \\ &= \frac{T_1/V_1}{T_1/V_1 + T_2/V_2} n_{abs} \end{aligned} \quad (\text{A.5})$$

where the equation was simplified considering that, to have a uniform pressure, $T_2/V_2 \cdot n_{2,in} - T_1/V_1 \cdot n_{1,in} = 0$.

The pressure variation after the gas absorption is given by:

$$\begin{aligned} \Delta P &= P_{in} - P_{fin} = \frac{n_{1,in}}{V_1} RT_1 - \frac{n_{1,fin}}{V_1} RT_1 = \\ &= \frac{RT_1}{V_1} (n_{abs} - n_{2-1}) \end{aligned} \quad (\text{A.6})$$

Substituting Equation A.5 for n_{2-1} , we have:

$$\begin{aligned} \Delta P &= \frac{RT_1}{V_1} \left(n_{abs} - \frac{T_1/V_1}{T_1/V_1 + T_2/V_2} n_{abs} \right) = \\ &= R \frac{T_1/V_1 \cdot T_2/V_2}{T_1/V_1 + T_2/V_2} n_{abs} \end{aligned} \quad (\text{A.7})$$

The final formula corresponds then to Equation 3.8. As shown in this section, this formula is obtained by applying the ideal gas law with the boundary conditions of a closed system with a spatially uniform pressure.

B List of Publications

1. **Guardi, G.**; Sarapulova, A.; Dsoke, S.; Wagner, S.; Pasquini, L.; Pundt, A. Controlled Hydrogen Loading of Magnesium Thin Films in KOH—Effects on the Hydride Nucleation and Growth Regimes. *Micro* 2024, 4, 765-777. <https://doi.org/10.3390/micro4040047>
2. Seiler, M.; **Guardi, G.**; Wagner, S.; Pundt, A. Applicability Range of Potential Step Chronoamperometry for Determining Reliable Diffusion Coefficients of Hydrogen and Lithium in Host Materials. *Electrochimica Acta* 2026, 546, 147790, <https://doi.org/10.1016/j.electacta.2025.147790>