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Hydrogen storage in binary and ternary Mg-based alloys: A comprehensive experimental study

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ABSTRACT

This study focused on hydrogen sorption properties of 1.5 μm thick Mg-based films with Al, Fe and Ti as alloying elements. The binary alloys are used to establish as baseline case for the ternary Mg–Al–Ti, Mg–Fe–Ti and Mg–Al–Fe compositions. We show that the ternary alloys in particular display remarkable sorption behavior: at 200 °C the films are capable of absorbing 4–6 wt% hydrogen in seconds, and desorbing in minutes. Furthermore, this sorption behavior is stable over cycling for the Mg–Al–Ti and Mg–Fe–Ti alloys. Even after 100 absorption/desorption cycles, no degradation in capacity or kinetics is observed. For Mg–Al–Fe, the properties are clearly worse compared to the other ternary combinations. These differences are explained by considering the properties of all the different phases present during cycling in terms of their hydrogen affinity and catalytic activity. Based on these considerations, some general design principles for Mg-based hydrogen storage alloys are suggested.

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1. Introduction

Hydrogen storage for mobile applications such as fuel-cell driven cars has been a very active research field for decades now. Because of its high gravimetric capacity of 7.6 wt%, MgH_2 has attracted a lot of attention as a suitable solid state storage medium. However, severe thermodynamic and kinetic limitations make high desorption temperatures around 300 °C necessary to release the stored hydrogen. Possible ways to improve the kinetics are alloying the Mg to alter the crystal structure of the hydride [1], reducing the particle and grain size by mechanical milling with e.g. nanostructured carbons [2] or by addition of catalytic additives such as Ni, LaNi_5 or La–Mg–Ni alloys during milling [3–5].

Thin films of Mg-based alloys are a subject of extensive research, as they are becoming increasingly more utilized for optical hydrogen sensing [6], switchable mirrors and solar absorbers [7], and as model systems for designing and understanding bulk hydrogen storage materials [1]. Mg–Ti, Mg–Al and Mg–Fe systems have been thoroughly investigated, because they have superior kinetics compared to pure Mg [8–13]. The behavior of the Mg–Ti system is quite complex in the sense that metastable alloys and hydrides can be formed. In-situ diffraction experiments at room-temperature showed that the formation of a cubic structure as opposed to rutile MgH_2 is responsible for the improved kinetics when the amount of Mg is below 80 at% [14,15]. However, DFT studies show that this structure is unstable relative to a mixture of the

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binary hydrides [16]. Therefore, the behavior of these alloys at the elevated temperatures necessary for full utilization of the capacity in solid–gas applications may be substantially different.

Bouaricha et al. reported favorable kinetics at 400 °C for $\text{Mg}_{0.9}\text{Al}_{0.1}$ and $\text{Mg}_{0.75}\text{Al}_{0.25}$ alloys [17]. Mg and Al were found to alloy upon desorption to form $\text{Mg}_{17}\text{Al}_{12}$. In accordance with the rule of reversed stability [18], the material was thermodynamically destabilized by 7 kJ/mol with respect to pure Mg. Bogdanovic et al. thoroughly investigated the Mg–Fe system at high temperatures. It was shown that formation of Mg_2FeH_6 is possible by prolonged absorption/desorption cycling of simple physical mixtures of MgH_2 and Fe, without ball-milling treatment. The cycling stability of the resulting material at 350 °C was excellent compared to pure Mg, because sintering of the Mg particles was strongly reduced [19].

While the performance of binary Mg-based alloys is clearly improved with respect to pure Mg, further reduction of the operating temperatures is desirable. Mg-based composites, consisting of Mg and additional hydride-forming/catalytic phases may be a viable route to achieve this. Liang et al. investigated Mg– LaNi_5 composites and reported 4.1 wt% reversible capacity and good cycling stability once the composite had transformed to its equilibrium state; a mixture of Mg, Mg_2Ni and LaH_3 [20]. Vijay et al. investigated composites of Mg and FeTi and FeTiMn prepared by ball-milling and found that the resulting materials could absorb over 4 wt% hydrogen in a few seconds at 200 °C and 30 bar [21]. Similar MgH_2 -5 wt% TiFeMn- 5 wt% V and Mg- 5 wt% LaNi_5 - 5 wt% Ti composite materials were investigated by Fu et al. who also performed cycle-life testing. The composite containing LaNi_5 and Ti displayed excellent cycling stability, whereas the Mg–TiFeMn–V composite showed severe degradation of the absorption kinetics in particular [22].

In view of the above, a systematic investigation of Mg-based composite materials with regard to storage capacity and cycling stability is desired. The goal of the present study is to find new Mg-based materials that can be rapidly and reversibly charged with hydrogen at low temperatures, while retaining constant capacity and kinetics over many tens of cycles. The alloys are fabricated in the form of 1.5 micron-thick sputter-deposited films. As a low temperature process, sputtering deposition enables the synthesis of metastable Mg alloy compositions. The binary Mg–Ti, Mg–Fe and Mg–Al systems are studied first, to establish a baseline case for the ternary systems. The tested ternary compositions cover all possible Mg-containing combinations of the binary alloys, i.e. Mg–Al–Ti, Mg–Fe–Ti and Mg–Fe–Al. Because of encouraging results on $\text{Mg}_{70}\text{Al}_{30}$ films [23–25], this Mg content was chosen as the starting point for the ternary alloys.

2. Experimental

Fig. 1A shows a schematic representation of how the material is built up. The Si substrates are 4 inches in diameter and covered with a layer of photoresist, which is applied by spin-coating. The photoresist layer enables separation of the sample from the substrate to obtain a free-standing film. This is important because it has been shown that clamping effects

can significantly alter the properties of thin layers of Mg [26,27]. The materials consist of an Mg-based storage layer of 1.5 μm thickness with a catalyst bilayer on top and bottom of the stack. Deposition was performed using a DC-magnetron co-sputtering system (AJA International). Deposition of the catalyst layers and of the bulk Mg alloy were performed sequentially without any interruption in a sputter-up configuration with continuous substrate rotation at room-temperature. The maximum base pressure was 5×10^{-8} mbar. During sputtering, Ar gas of 5 N purity was used at a pressure of 4 mTorr.

For the main storage layer, the individual deposition rates have to be adjusted to obtain the desired alloy compositions. Mg was deposited at a power level of 100 W, which corresponded to a deposition rate of 2.5–2.9 Å/s. Prior to deposition of the sample, the deposition rates of Ti, Al, and Fe were determined for three different power levels and used as a calibration curve. To obtain the desired alloy stoichiometries, the deposition rates from the rate tests were converted to mol/unit area/second and the appropriate power levels for Ti, Al and Fe were derived from the calibration curves. The total deposition rate was always around 4 Å/s.

At the bottom and top of the stack, a catalyst bilayer consisting of 7.5 nm Ta/7.5 nm Pd is deposited at a rate of 1.5 Å/s. This catalyst layer protects the bulk storage layer from oxidation and catalyzes the dissociation of hydrogen. Neutron Reflectometry studies on thin $\text{Mg}_{70}\text{Al}_{30}$ films with only a 10 nm Pd cap layer showed that the Pd layer had fully interdiffused with the $\text{Mg}_{70}\text{Al}_{30}$ film after annealing for 9 h at 200 °C [23]. Experiments on Mg layers with a single Pd catalyst layer revealed that this alloying of Pd with the Mg storage layer should be avoided. We tested several bilayer catalyst combinations on pure Mg at 250 °C and Pd/Ta showed best performance [28]. Therefore, an additional Ta layer was used to prevent or slow down the interdiffusion of the catalytic Pd with the hydrogen storage layer. It should be noted here that the Ta/Pd bilayer catalyst makes up 10–15 wt% of the sample mass.

After deposition, the photoresist layer is dissolved in acetone and a free-standing film is obtained that is used for further testing. SEM micrographs of what the films typically look like after absorption/desorption cycling are also shown in Fig. 1B–D. The films retain their plate-like morphology as shown in Fig. 1B and C. In Fig. 1D, these plates are seen to form large aggregates whose dimensions are similar to those of powders, which means these micron-thick films are very good model systems for bulk powders in terms of diffusion distances and surface to volume ratios.

Ab- and desorption kinetic measurements were performed at 200 °C in a Sieverts type apparatus (HyEnergy Scientific Instruments PCTPro2000). Typical sample mass was 15–20 mg. For cycling tests, the pressure in the reservoir (volume: 11.9 ml) was set to 3 bar for absorption. The final pressure at the end of the absorption step was around 1.5 bar. For desorption, the reservoir (1025 ml) was initially put under primary vacuum. Expansion of the hydrogen present in the sample holder after absorption resulted in a starting pressure for desorption of approximately 5 mbar, which increased to 15–20 mbar near the end of the desorption step. The ab- and desorption steps were terminated when an average rate lower

Fig. 1 – A: Schematic picture of Mg alloy films with catalyst layers. B: SEM picture of individual alloy flake after cycling. C: close-up of flakes' edge D: large powder-like aggregate of plate-like fragments.

than 0.005 wt%/min was measured over a period of 4 min. After desorption, the samples were evacuated for another 5 min before the next absorption step.

X-ray diffraction experiments were performed on a Bruker AXS diffractometer (Bruker Discover 8) using a Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$) that was monochromatized using a single Göbel mirror. The diffractometer is equipped with a HiStar general area 2-dimensional detection system (GADDs) with a sample–detector distance of 15 cm. The data from the XRD database on EVA software were used for peak identification. The number from the Powder Diffraction File will be given as a reference in the results section. The XRD patterns of the absorbed $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ samples were measured with a Rigaku Ultima III X-ray diffractometer, in high resolution configuration (Cu-K α 1 $1.5406 \text{ \AA}$). A crystal analyzer was also used to reduce the contribution of diffuse scattering and background.

3. Results

3.1. Binary alloys

3.1.1. $\text{Mg}_{70}\text{Al}_{30}$

The desorption temperature of 50 nm $\text{Mg}_{1-x}\text{Al}_x$ films using a Ta/Pd bilayer catalyst can be as low as 100°C as compared to 175°C for films with only a single Pd layer. However, desorption times are very long under those conditions [24,25]. Fig. 2A and B show the absorption and desorption behavior at 200°C of a $\text{Mg}_{70}\text{Al}_{30}$ film capped with a Ta/Pd bilayer catalyst. The total capacity of the alloy is initially slightly more than 4 wt%, which agrees well with values found in our previous studies [23–25]. The time it takes to ab-or desorb 3 wt% of hydrogen as a function of cycle number is depicted in Fig. 2C. The desorption time increases only very slightly upon extended cycling for more than 25 cycles. The absorption time on the

other hand increases much more strongly. For the first 10 cycles, the absorption time to 3 wt% is approximately constant at 15 min, which is slightly faster than the desorption time. After 10–15 cycles, however, the time-to-3 wt% starts to increase steadily, up to 45 min at the 29th cycle.

A possible explanation for this behavior can be found in the XRD patterns that were collected in the course of cycling (see Fig. 3). In the as-deposited state, the Mg and Al exist as a solid solution. The Mg (002) reflection is shifted to $2\theta = 35.05^\circ$, a considerably higher angle compared to the value of 34.4° of pure Mg. In equilibrium, a maximum of 11.5 at% Al can be dissolved in Mg at 437°C and only 1 at% at 100°C [29], which means the as-deposited state of the film is metastable. The composition $\text{Mg}_{70}\text{Al}_{30}$ falls within the 2-phase region between Mg(Al) solid solution and $\text{Mg}_{17}\text{Al}_{12}$ intermetallic.

Upon absorption, the as-deposited alloy is transformed into a mixture of α and γ - MgH_2 and Al metal. Subsequent desorption leads to the formation of the $\text{Mg}_{17}\text{Al}_{12}$ intermetallic (1-1128 Space group I-43 m, $a = 10.58 \text{ \AA}$), which is closer to the equilibrium state of the system. After the 10th absorption, the γ - MgH_2 phase is no longer observed, leaving only the equilibrium α - MgH_2 and Al metal. Around 38° , an amorphous halo is observed. Finally, after 29 ab-and desorption cycles, Mg, $\text{Mg}_{17}\text{Al}_{12}$ and Mg_6Pd (25-1084 space group F-43 m, $a = 20.108 \text{ \AA}$) are found. The formation of Mg_6Pd coincides with a steady deterioration of the absorption kinetics from the 10th cycle onwards, where the time to absorb 3 wt% eventually increases by a factor 3. The desorption time is much less affected. This agrees well with the earlier observation that the formation of Mg_6Pd is detrimental to the kinetics [25,28]. Apparently, despite the presence of a Ta interlayer, Mg and Pd can still react to form this intermetallic at 200°C .

3.1.2. $\text{Mg}_{70}\text{Fe}_{30}$

$\text{Mg}_{70}\text{Fe}_{30}$ absorbs 4.8 wt% in the first cycle (see Fig. 4A), but subsequent cycles show that only 0.6–0.8 wt.% is reversible at

Fig. 2 – Hydrogen ab- and desorption data of a 1.5 μm thick $\text{Mg}_{70}\text{Al}_{30}$ film capped with Ta and Pd. A: 1st, 5th, 10th and 25th absorption cycle B: 1st, 5th, 10th and 25th desorption cycle of the same material as in A. C: Evolution of the time it takes to ab- and desorb 3 wt%. Note how after 10 cycles, the absorption time starts to increase, eventually by a factor 3.

200 °C. The XRD pattern of the as-deposited film shows no shift in the Mg (002) peak, contrary to $\text{Mg}_{70}\text{Al}_{30}$, indicating that Fe does not dissolve in Mg. In its fully absorbed state, the material has formed a mixture of a very small amount of MgH_2 and mainly consists of Mg_2FeH_6 (75–675 space group Fm-3 m, $a = 6.43 \text{ \AA}$). This could be expected as the overall stoichiometry of the film is very close to Mg_2Fe . The very small reversible capacity means that only the MgH_2 is cycleable. This is most likely due to the relatively low temperature that was applied in the present study. Bogdanovic et al. were able to fully utilize the capacity of Mg_2FeH_6 at temperatures above 350 °C, with

Fig. 3 – XRD patterns upon cycling for $\text{Mg}_{70}\text{Al}_{30}$. A: XRD patterns in as-deposited state and after the 1st and 3rd cycle. Note the transition from metastable solid solution in the as-deposited state to formation of equilibrium $\text{Mg}_{17}\text{Al}_{12}$ intermetallic after first few desorption cycles. B: XRD patterns of $\text{Mg}_{70}\text{Al}_{30}$ after 10 and 29 cycles. Upon extended cycling, Mg_6Pd intermetallic appears in the diffraction pattern. The $\text{Mg}_{17}\text{Al}_{12}$ peaks are indexed.

excellent cycling stability up to 600 cycles [19]. From their data, an enthalpy of formation for Mg_2FeH_6 of -77.4 kJ/mol H_2 and an entropy change of -134 J/mol/K can be estimated, which gives an equilibrium pressure from the Van 't Hoff equation [30]

$$\ln \frac{P}{P_0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (1)$$

of 33 mbar. Hence, it should be possible to desorb Mg_2FeH_6 under our experimental conditions, but this does not happen, most likely because of kinetic limitations.

3.1.3. $\text{Mg}_{75}\text{Ti}_{25}$

The ab- and desorption behavior of a $\text{Mg}_{75}\text{Ti}_{25}$ alloy is shown in Fig. 5A and B. Initially, the material absorbs 5.2 wt%, but only

Fig. 4 – Absorption cycles and XRD patterns of $\text{Mg}_{70}\text{Fe}_{30}$
A: 1st, 5th and 30th absorption cycle of 1.5 μm thick $\text{Mg}_{70}\text{Fe}_{30}$ film capped with Ta and Pd. Note the large difference between the first and subsequent absorption capacities. **B:** XRD patterns of as-deposited and fully absorbed $\text{Mg}_{70}\text{Fe}_{30}$.

3.6 wt% is reversible. The desorption rate is very fast initially; in cycle 1 and 5, the first 2 wt% is desorbed at a rate of approximately 1 wt%/min. After 25 cycles, the desorption kinetics have clearly deteriorated compared to the first 5 cycles. Apparently, the elevated temperature in the present study has a profound effect on the behavior of this material. Previous room-temperature tests of this material as an active layer for hydrogen sensors [6] and as an electrochemical storage medium [8,9] revealed excellent cycling stability. This has been attributed to the fact that Mg and TiH_2 have almost the same molar volume, enabling formation of a coherent fcc structure [14,15] that can be reversibly hydrided and dehydrided.

However, DFT studies have shown that the ternary, cubic hydride that is formed at room-temperature is metastable with respect to a mixture of the binary hydrides [16]. The XRD patterns of the as-deposited, fully absorbed and fully desorbed $\text{Mg}_{75}\text{Ti}_{25}$ shown in Fig. 6 corroborate this. In the as-deposited state, the Mg and Ti form a complete solid solution with strong preferential orientation in the (002) direction, the same as the Mg–Al system. The XRD patterns after cycling at 200 °C show that the material gradually decomposes. After 7 cycles, traces

Fig. 5 – Selected ab- and desorption cycles of 1.5 μm thick $\text{Mg}_{75}\text{Ti}_{25}$ film capped with Ta and Pd. A: 1st, 5th and 25th absorption cycle. Note the large irreversible part of the capacity in the first cycle, roughly corresponding to 2 H/Ti. **B:** 1st, 5th and 25th desorption cycle of $\text{Mg}_{75}\text{Ti}_{25}$.

of Mg metal and Mg_6Pd are detected. From the positions of the remaining reflections and the corresponding d -values, it can be derived that the major part of the material consists of a fcc phase (Space group $\text{Fm}\bar{3}\text{m}$) with a lattice constant of 4.50 Å, close to the lattice constant of TiH_2 .

Upon extended cycling, the material decomposes further into the binary hydrides. After 25 cycles, the fully absorbed material consists mainly of a mixture of Mg_6Pd , MgH_2 and TiH_2 . The same fcc structure is detected with a lattice constant of 4.59 Å. For fully hydrogenated $\text{Mg}_{70}\text{Ti}_{30}$ and $\text{Mg}_{80}\text{Ti}_{20}$, Vermeulen et al. reported fcc phases with $a = 4.66$ and 4.71 Å, respectively [15]. The difference in lattice constant is consistent with the segregation of a considerable amount of MgH_2 , which would decrease the molar volume of the ternary hydride phase.

To definitively determine whether the fcc phase is TiH_2 , as the irreversible capacity after the first absorption seems to suggest, or a phase similar to the metastable fcc phases reported by Vermeulen et al. [15], a different sample with the same composition was cycled 3 times and subsequently annealed at 300 °C in the fully absorbed state for 8 hours. Mg, Mg_6Pd and MgH_2 are clearly present in the diffraction pattern. The reflections of TiH_2 and the fcc phase are at the same

Fig. 6 – XRD patterns of $\text{Mg}_{75}\text{Ti}_{25}$ in the as-deposited state, desorbed after 7 cycles and absorbed after 25 cycles. Notice how after the initial formation of a metastable fcc phase, the material has partially decomposed into the binary hydrides. Extended cycling and annealing appear to have the same effect.

positions as after 25 cycles at 200 °C and both differ from the fcc phase found in the desorbed state after 7 cycles. Hence, initially, a metastable fcc phase is formed, which decomposes into the binary hydrides upon further cycling.

All binary systems studied so far have some clear disadvantages. The kinetics and capacity of $\text{Mg}_{75}\text{Ti}_{25}$ deteriorate due to the metastable nature of the fcc hydride phase. $\text{Mg}_{70}\text{Al}_{30}$ showed deterioration of the absorption kinetics by a factor 3 and the Mg_2FeH_6 was irreversible in binary $\text{Mg}_{70}\text{Fe}_{30}$. Extension to ternary systems is a possible way to solve these problems. From electrochemical experiments, it is known that formation of a multiphase composite material can greatly improve the kinetics of Mg-based materials, even at room-temperature [31]. Combining Mg–Ti with Al or Fe will very likely result in the formation of composite materials consisting of $\text{Mg}(\text{H}_2)$ and a secondary AlTi or FeTi phase, because Ti interacts much more strongly with Al or Fe than with Mg [32].

3.2. Ternary alloys

3.2.1. Mg–Ti–Al

Fig. 7A and B depict the 1st, 5th, 10th, 50th and 100th absorption and desorption cycles, respectively, for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$. Only the first absorption cycle is relatively slow, taking over 20 min to complete, but subsequent cycles show extremely fast absorption in the order of seconds. For desorption, the kinetics stabilize after approximately 10 cycles, when complete desorption takes approximately 15 min to complete. The material has a total capacity in desorption of slightly more than 4 wt%, which is approximately equal to what would be expected based on ab-and desorption cycling of Mg alone.

As Fig. 7C illustrates, absorption is extremely fast compared to desorption. The unit on the left hand axis, where

Fig. 7 – A: Absorption cycle 1, 5, 10, 50 and 100 of $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$. B: Desorption cycle 1, 5, 10, 50 and 100. C: Time to reach 3.5 wt.% absorption in seconds (left hand y-axis) and 3.5 wt.% desorption in minutes (right-hand y-axis).

the time to absorb 3.5 wt% (i.e. 85% of the total capacity) is plotted, is seconds, whereas the desorption time (right-hand y-axis) is in minutes. This behavior is completely different from e.g. the $\text{Mg}_{70}\text{Al}_{30}$ alloy, where the timescales for ab-and desorption were comparable. The ab-and desorption rates remain stable up to at least one hundred cycles, as Fig. 7C also illustrates. The absorption time to 3.5 wt% is stable around 5–6 s; desorption to the same wt% takes 10–11 min at steady state.

In the as-deposited state, Al and Ti have complete solid solubility in Mg as is evident from the XRD patterns in Fig. 8. The Mg (002) reflection is at 35.9° , which is close to the 35.7° reported for $\text{Mg}_{70}\text{Ti}_{30}$ [15]. As Mg and Ti have virtually zero solid solubility in equilibrium, the as-deposited state of the film is, the same as $\text{Mg}_{70}\text{Al}_{30}$, metastable. After 80 cycles, a mixture of Mg and MgH_2 , Mg_5Pd_2 (22-713 space group P63/mmc, $a = 8.6598 \text{ \AA}$, $c = 8.1688 \text{ \AA}$) and TiAl (65-428 space group P4/mmm, $a = 4.001 \text{ \AA}$, $c = 4.071 \text{ \AA}$) is found. The Mg–Pd intermetallic is only present in small amounts, which makes it very hard to conclusively determine which phase is present. The small reflections around 26 and 41° either belong to Mg_5Pd_2 or Ti_3Al (52-859 Space Group P63/mmc, $a = 5.793 \text{ \AA}$, $c = 4.649 \text{ \AA}$). Ti_3Al would not be expected to form based on the overall stoichiometry of the alloy, but a small error during deposition or reaction of Al with Ta or Mg would put the Ti/Al ratio in the two-phase region between Ti_3Al and TiAl.

To determine more conclusively which phases are formed, a sample capped with only 1.5 nm of Pd, to limit the amount of Mg–Pd intermetallic that is formed was cycled under the same conditions as the film capped with 7.5 nm Pd. In an attempt to improve the crystallinity of the material and gain more clarity on the phases present that way, a sample capped with 7.5 nm Pd was cycled at 250°C instead of 200°C . The diffraction patterns of the resulting materials are also shown in Fig. 8. Besides diffraction peaks of Mg and a very broad peak around 38° , no other phases are detected in either pattern. It is therefore most likely that the minor reflections observed after 80 cycles at 200°C are due to Mg_5Pd_2 and not Ti_3Al and that TiAl is the only Ti–Al intermetallic present during cycling.

Increasing the amount of Mg in the alloy will of course increase the capacity in wt% H of the material. However, the important question is then whether the favorable kinetic properties will be preserved. For $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$, the hydrogen

Fig. 8 – XRD patterns of as-deposited and cycled $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$. Note the large shift of the Mg (002) peak in the as-deposited state, indicating complete solid solubility of Al and Ti. After 80 cycles, when the material is fully activated, AlTi and Mg–Pd intermetallics are found as well. Cycling at higher temperatures (250°C) and using less Pd both result in complete dissolution of the Pd.

cycling data are shown in Fig. 9. Similar to $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, the first absorption cycle is considerably slower than subsequent cycles, but after 10 cycles, the system has basically reached its steady state. As for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, the desorption time takes considerably longer to stabilize and keeps improving significantly up to the 20th cycle. The material desorbs 5.4 wt% before the desorption rate becomes lower than the cut-off criterion of 0.005 wt%/min, which is, once again, approximately equal to the expected value based on reversible ab-and desorption of 2 H/Mg (5.6 wt%). The absorption rate is, the same as for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, extremely high compared to desorption. The time to 4.5 wt% (85% of total) is plotted in Fig. 9C for both ab-and desorption. Absorption times are as short as 8s and remain stable up to 100 cycles. The desorption

Fig. 9 – Cycling kinetic data for $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$ A: Absorption cycle 1, 5, 10 and 50. B: Desorption cycle 1, 5, 10, 50 and 100. C: Time to reach 4.5 wt% absorption in seconds (left hand y-axis) and 4.5 wt% desorption in minutes (right-hand y-axis).

Fig. 10 – XRD patterns of $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$. The lattice parameters in the as-deposited state are estimated as $a = 3.17 \text{ \AA}$ and $c = 5.12 \text{ \AA}$. Note how the Mg metal peaks have shifted back to the positions of pure Mg after 20 cycles. The patterns after 20 and > 100 cycles look virtually identical and show peaks of $\text{Mg}(\text{H}_2)$, AlTi and Mg_5Pd_2 . As for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, cycling at 250°C completely dissolves the Pd, leaving only Mg and a broad peak where the main AlTi peak is expected.

time to 4.5 wt% stabilizes at approximately 15 min after the first 20 cycles, which is slightly slower than the desorption time for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$. The same as for the absorption time, this value remains stable up to at least 100 cycles.

Fig. 10 depicts the XRD patterns of $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$ in the as-deposited state, fully absorbed state after 20 cycles and fully desorbed state after >100 cycles. Similar to $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, full solid solubility of the Al and Ti in Mg is achieved for the as-deposited state. Contrary to $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, this film could be easily crushed, enabling the recording of a more powder-like pattern. Based on the peak positions for the hexagonal Mg phase, the lattice constants are estimated as $a = 3.17 \text{ \AA}$ and $c = 5.12 \text{ \AA}$. From these lattice parameters, a molar volume of $13.4 \text{ cm}^3/\text{mol}$ is calculated, which is the same as what would be expected based on the molar volumes of the constituent elements. The same phases found in the $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$ alloy after 80 cycles are also formed after 100 cycles in the $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$ alloy. The diffraction patterns after 20 and >100 cycles are virtually identical, apart from the difference between absorbed and desorbed state. The same as for $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$, a sample was cycled at 250°C to determine which phases evolve at higher temperature. Again, the only reflections that are visible in the diffraction pattern belong to Mg and TiAl.

3.2.2. Mg–Fe–Ti

Figs. 11 and 12 show the ab- and desorption behavior of $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$. The reversible capacity in steady state equals 4 and 5 wt% for $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$, respectively, which corresponds to approximately 2 H/Mg in both cases. PCT measurements performed in

Fig. 11 – Hydrogen cycling data for $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$. A: Absorption cycle 1, 5, 10 and 50. Notice that steady state is reached after only 5 cycles B: Desorption cycle 1, 5, 10, 50, 100 and 106 C: Time to reach 3.5 wt% absorption in seconds (left hand y-axis) and 3.5 wt% desorption in minutes (right-hand y-axis).

a dedicated study on this system revealed that its thermodynamic properties are identical to pure Mg [33], which supports the assumption that only Mg is being cycled. Both compositions show an initial activation period, similar to the Mg–Al–Ti alloys, where the kinetics are considerably slower and the capacity somewhat higher than in steady state. The activation period lasts for approximately 10–15 cycles, where the time to absorb 3.5 wt% for $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and 4.5 wt% for $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$ improves by a factor 100 between the first and 15th cycle. For desorption, the relative difference between the first cycle and steady state is much smaller; about a factor 2 for both compositions. Upon extended cycling, no degradation of

Fig. 12 – Hydrogen cycling data for $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$.
A: Absorption cycle 1, 5, 10 and 50. Steady state is attained within 5 cycles
B: Desorption cycle 1, 5, 10, 50 and 100
C: Time to reach 4.5 wt% absorption in seconds (left hand y-axis) and 4.5 wt% desorption in minutes (right-hand y-axis).

either the capacity or the kinetics is apparent up to more than 100 cycles for both $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$.

Fig. 13 depicts the XRD patterns of as-deposited $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and a fully absorbed $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$ alloy after 100 cycles. In the as-deposited state, the Mg (002) reflection is clearly shifted towards higher angles, indicating at least partial solid solution behavior. However, contrary to the Mg–Al–Ti films, the observed shift of the Mg (002) reflection is much smaller than expected based on the average molar volume of the constituent elements. This indicates that part of the Fe and Ti is deposited as a separate phase. In equilibrium, neither Fe nor Ti has any appreciable solubility in Mg, which means the part of Fe and Ti that is dissolved initially is

Fig. 13 – XRD patterns of as-deposited $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ and absorbed $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$ after 100 cycles. The Mg (002) peak is shifted in the as-deposited state for $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$, although the shift is smaller than expected (34.9°). After cycling, the only crystalline phase that is detected is MgH_2 .

expected to segregate upon hydrogen loading. However, the XRD pattern of the fully absorbed $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$ alloy shows no crystalline phases besides the equilibrium $\alpha\text{-MgH}_2$ phase. Apparently, the FeTi intermetallic, whether it is present in the as-deposited state or precipitates from solid solution upon cycling, remains amorphous throughout the entire duration of the experiment.

3.2.3. Mg–Al–Fe

For the Mg–Al–Fe system, two different compositions are presented: $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$. The Mg–Al–Fe system differs from the Mg–Al–Ti and Mg–Fe–Ti systems in that both alloying elements have a very low affinity for hydrogen. AlH_3 has an enthalpy of formation of -8 kJ/mol H_2 and for $\text{FeH}_{0.5}$ this value is $+20 \text{ kJ/mol H}_2$, whereas the formation enthalpy of TiH_2 equals -136 kJ/mol H_2 [30]. However, AlFe has an enthalpy of formation of -25 kJ/mol [32] and the presence of Al could therefore improve the reversibility of Mg_2FeH_6 at lower temperatures by slightly destabilizing the hydride.

A selected number of ab- and desorption cycles is shown in Figs. 14 and 15 for $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$, respectively. Although the compositions differ little, the Fe/Al ratio is increased from 1.5 to 2, the hydrogen cycling behavior is quite different. For both compositions, the material absorbs hydrogen very slowly in the first cycle. The total absorption capacity in the first cycle is 3.5 wt% for $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and 4.13 wt% for $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$, but the alloys absorb only 1.7 and 2.6 wt%, respectively, in the first hour.

Contrary to the Mg–Al–Ti and Mg–Fe–Ti systems, the kinetics and capacity rapidly degrade upon cycling for $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$. The 10th absorption is noticeably slower than the previous cycles and the 10th desorption took a little over 7 h to complete. After the 10th cycle, the material once more absorbed 2.6 wt% in 10 min, but showed hardly any activity after that. For $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$, the capacity rapidly decreases in the initial stages of cycling, but after 10–15 cycles, the capacity stabilizes at 1–1.5 wt% for many tens of cycles, as opposed to

Fig. 14 – Hydrogen cycling data for $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ A: 1st, 2nd, 5th, 10th and 16th absorption cycle. B: 1st, 2nd, 5th, 10th and 16th desorption cycle. Note that the 10th desorption is extremely slow after which the material becomes inactive.

$\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$, where only 0.15% is reversible in later stages of cycling. It has to be noted, however, that the kinetics for this alloy are significantly slower compared to the Mg–Al–Ti and Mg–Fe–Ti alloys. Absorption of only 1 wt% (2/3 of the total capacity) already takes more than 1 min, whereas $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ absorbs over 80% of its total capacity in 5–10 s (see Fig. 11C).

An explanation for the difference in sorption behavior between $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ can be found in the XRD patterns in Figs. 16 and 17. Contrary to the Mg–Al–Ti and Mg–Fe–Ti alloys, the as-deposited $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ alloy does not exhibit any shift in the position of the Mg (002) peak, which is found exactly where it is expected for pure Mg at 34.4° . Apparently, the Mg–Fe–Al compositions tested here are already segregated into Mg and an intermetallic phase in the as-deposited state. In absorbed state after cycling, $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ contains a small amount of Mg_2FeH_6 , Mg_5Pd_2 , MgH_2 and FeAl (33-20 space group Pm-3 m $a = 2.8954 \text{ \AA}$) or Fe_3Al (65-3006 space group Fm-3m, $a = 5.7922 \text{ \AA}$) intermetallic. The absorbed $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ alloy on the other hand, contains MgH_2 , FeAl/ Fe_3Al intermetallic and a much larger amount of Mg_2FeH_6 . No Mg–Pd intermetallic can be discerned in the diffraction pattern. In the desorbed state, the amount of Mg_2FeH_6 is drastically reduced in $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ showing that, contrary to the binary $\text{Mg}_{70}\text{Fe}_{30}$, Mg_2FeH_6 can be reversibly hydrided and dehydrided. The presence of Al is the most likely

Fig. 15 – Ab- and desorption cycles for $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ A: 1st, 2nd, 10th and 45th absorption cycle. Note that for this composition, 1.5 wt% remains cycleable. B: 1st, 2nd, 10th and 45th desorption cycle.

Fig. 16 – XRD patterns of as-deposited and absorbed (10 cycles) $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$. In the as-deposited state, no shift of the Mg (002) peak is detected. After cycling, the material consists of FeAl, Mg_5Pd_2 , MgH_2 and a minor amount of Mg_2FeH_6 .

Fig. 17 – XRD patterns of as-deposited, absorbed and desorbed $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$. Note that the Mg (002) peak is exactly where it is expected for pure Mg, the same as for $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$. Upon cycling, a much larger amount of Mg_2FeH_6 is formed, which is reversible, contrary to binary $\text{Mg}_{70}\text{Fe}_{30}$.

cause for this difference. In the presence of Al, the Fe released from Mg_2FeH_6 can be dissolved in FeAl intermetallic that is already present. The solubility limits of FeAl/ Fe_3Al in the Fe–Al phase diagram range from $\text{Fe}_{50}\text{Al}_{50}$ to as far as $\text{Fe}_{75}\text{Al}_{25}$ at 400 °C, so a Fe/Al ratio of 2 falls well within that region [29].

The FeAl intermetallic is always present in the diffraction pattern, despite the fact that there is enough Mg in $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ to fully convert the Fe into Mg_2FeH_6 . The enthalpy of formation of FeAl of -25 kJ/mol would raise the enthalpy of hydrogenation of Mg and Fe to Mg_2FeH_6 by 8 kJ/mol H_2 , since there are 3 mol of H_2 for every mole of Fe in Mg_2FeH_6 . Using the Van 't Hoff equation, assuming the same value for ΔS derived from ref. [19], an equilibrium pressure of 150 mbar can be calculated, which is much lower than the absorption pressure used in our experiments. So in principle, the FeAl can be completely converted to Mg_2FeH_6 and Al upon hydrogenation, but this does not happen because of kinetic limitations. In fact, the theoretical maximum capacity for $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ based on:

would be 4.39 wt%, when the weight of the catalyst layers is taken into account. This is very close to the experimentally measured value of 4.13 wt%.

4. Discussion

Comparing all the data on the different alloy systems, some general observations can be made. Alloys where either the absorption or desorption step involves formation or decomposition of an intermetallic are kinetically much slower compared to alloys where Mg is simply being hydrided and dehydrided. Compared to the ternary Mg–Al–Ti and Mg–Fe–Ti systems, absorption in $\text{Mg}_{70}\text{Al}_{30}$ is very slow; 15 min vs. less

than 15 s. When MgH_2 is formed from the Mg–Al intermetallic phase according to:

two new phases, MgH_2 and Al must nucleate from the intermetallic phase. This involves long-range diffusion of Al atoms, which is much slower than diffusion of hydrogen or a simple rearrangement of the Mg atoms from hcp to tetragonal. The same is true for the $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ alloy, where Fe atoms must diffuse from the AlFe intermetallic phase to form Mg_2FeH_6 and diffuse back into the intermetallic upon desorption.

A major difference between the Mg–Al–Fe and the Mg–Al–Ti and Mg–Fe–Ti systems is that Mg–Al–Fe is already segregated in the as-deposited state, whereas the latter two systems are, at least partially, in solid solution. Because Fe and Ti have no appreciable equilibrium solubility in Mg, decomposition of the alloys creates a highly dispersed composite material of Mg and an intermetallic phase. Because FeTi is a hydride former, and AlTi also has a significant, although small, hydrogen solubility they can act as a rapid diffusion path for hydrogen during absorption and desorption. This is further corroborated by the fact that reducing the amount of AlTi and FeTi leads to a deterioration of the kinetics; most notably for the initial desorption cycles of $\text{Mg}_{85}\text{Fe}_{7.5}\text{Ti}_{7.5}$. Both Al and Fe, on the other hand, have very low hydrogen affinity and therefore AlFe is not expected to be able to create a diffusion path for hydrogen through the bulk of the material in the same way as FeTi and AlTi. This is especially clear during the very first absorption cycle, where the kinetics of $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ and $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$ are an order of magnitude slower compared to e.g. $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$.

For pure Mg layers, a previous study has shown that the Pd catalyst will always react with Mg to form Mg_6Pd , despite the presence of either Fe, Ti, Nb or Ta as a barrier layer between the Pd layer and the Mg layer [28]. Indeed, the XRD patterns of all cycled Mg–Al, Mg–Al–Ti alloys and $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ proved the presence of Mg_6Pd or Mg_5Pd_2 , which will worsen the sorption kinetics. However, the secondary TiAl and FeTi phases, are able to take over the role of Pd as a catalyst, as both Fe and Ti are catalytic towards hydrogen dissociation. Apparently, the FeAl intermetallic does not have this catalytic activity, which causes the sudden deactivation of $\text{Mg}_{70}\text{Al}_{12}\text{Fe}_{18}$ after 10 cycles, when all the active Pd has reacted with Mg.

Another general observation is that for the Mg–Al–Ti and Mg–Fe–Ti absorption is 2 orders of magnitude faster than desorption; e.g. 6 s vs. 11 min for 3.5 wt% H in $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$. For FeTi the heat of hydride formation is -28 to -35 kJ/mol H_2 (multiple plateaus) [34]. From the Van 't Hoff equation, the equilibrium pressure at 200 °C is calculated to be 0.9 kbar, so none of the FeTi hydrides will be stable at 3 bar. TiAl, does not form a hydride and the hydrogen solubility is in the order of 1 ppm by weight [35]. Hence, it seems that especially dilute hydride phases promote the rapid uptake of hydrogen in Mg. This agrees qualitatively with the experimental results obtained by Pasturel et al. on Pd/TM/ Mg_2Ni trilayers [36]. They observed the highest absorption rates at room-temperature for TM = Pd and Mn, while for TM = Ti and V, which form more concentrated hydrides, the absorption kinetics were markedly slower. For desorption, an opposite trend was observed. To study this in more detail, experiments on multilayered systems, where the secondary

hydride-forming phase truly acts as a barrier between Mg layers are in progress.

The binary $\text{Mg}_{75}\text{Ti}_{25}$ alloy represents a somewhat special case. The initial desorption rate for the first 5 cycles is (see Fig. 5B) $> 1 \text{ wt\%/min.}$, which is higher than for any of the ternary compositions. XRD showed that after a limited number of cycles (7), the major part of the material consists of a ternary fcc phase, similar to what is found in room-temperature experiments. This fcc phase is present both in the desorbed and absorbed state, showing that this material can be reversibly hydrided and dehydrided while keeping the host lattice structure the same. However, the metastable nature of the ternary hydride, as evidenced by the gradual decomposition into MgH_2 and TiH_2 , makes the cycling stability of this alloy unsatisfactory.

5. Conclusions

Binary and ternary Mg-based alloys with Fe, Al and Ti as alloying elements have been studied. The binary $\text{Mg}_{70}\text{Al}_{30}$ and $\text{Mg}_{75}\text{Ti}_{25}$ alloys showed degradation of the kinetics over time because of alloying of the Ta and Pd catalyst layers or decomposition of a metastable ternary hydride phase. In binary $\text{Mg}_{70}\text{Fe}_{30}$, Mg_2FeH_6 can be formed, but is not reversible at 200°C . The ternary alloys show superior performance over the binary ones. This is very likely due to their multiphase structure, combining Mg as the main storage phase with Ti–Al or Ti–Fe intermetallics as pathways for enhanced hydrogen diffusion and surface catalysts. Kinetically, the $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$ and $\text{Mg}_{70}\text{Fe}_{15}\text{Ti}_{15}$ show the best performance, fully desorbing their total capacity of approximately 4 wt% within 15 min, which remains stable for over 100 cycles. The Mg–Al–Fe alloys, which do not form a hydride-forming secondary phase, perform considerably worse, although the presence of Al makes Mg_2FeH_6 cyclable in $\text{Mg}_{70}\text{Al}_{10}\text{Fe}_{20}$. Of all the compositions that were tested, $\text{Mg}_{85}\text{Al}_{7.5}\text{Ti}_{7.5}$ has the highest reversible capacity of 5.4 wt% and performs kinetically only slightly worse than $\text{Mg}_{70}\text{Al}_{15}\text{Ti}_{15}$.

Summarizing, some general design principles for Mg-based composite hydrogen storage materials can be formulated:

1. Long-term cycling stability in terms of capacity and kinetics is achieved only when the material is in its thermodynamically most stable state; i.e. a mixture of a main storage phase, Mg, and a stable intermetallic acting as a catalyst and/or diffusion path. The occurrence of a metastable phase, such as the fcc phase in Mg–Ti, deteriorates the kinetics over time.
2. The secondary/catalytic phase should contain at least one element with high affinity for hydrogen. The Ti-containing systems tested in the present study showed far superior performance over Mg–Al–Fe.
3. Reactive systems where an Mg alloy ($\text{Mg}_{17}\text{Al}_{12}$) or Mg-based ternary hydride (Mg_2FeH_6) is formed are intrinsically slower than simple hydrogenation/dehydrogenation of Mg.

At the pressures used in the present study, the hydrogen concentration in FeTi and AlTi is low. Possibly, the extremely fast absorption rate as compared to desorption is related to

this low hydrogen concentration. Further studies on multi-layered systems, where the composition of the material between the Mg layers is tuned to obtain either concentrated or dilute hydrides in the pressure regime around 1 bar will be used to elucidate the effects of the hydrogen concentration in the secondary phase on the ab- and desorption kinetics.

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