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# Hydrogen storage in magnesium-metal mixtures: Reversibility, kinetic aspects and phase analysis

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#### Abstract

The sorption capacity and kinetics of mechanically activated binary mixtures of Mg with nine different metals (Al, Cu, Fe, Mn, Mo, Sn, Ti, Zn, Zr) have been studied to determine whether these metals act as catalyzing/destabilizing agents in formation/decomposition of Mg hydrides. Identification of crystalline phases before and after the absorption/desorption processes assists our understanding of the different behaviors displayed by the studied compounds. Cu, Al and Zn take active part in Mg hydrogenation/dehydrogenation, but only the addition of Cu is actually effective in MgH<sub>2</sub> destabilization, leading to a substantial decrease of the desorption temperature of this phase (down to 270 °C), and to an improved desorption kinetics. With the other metals, the hydrogen release usually occurs at a significant rate only above 320 °C and the kinetics of the absorption/desorption processes are slower than in the Mg/MgH<sub>2</sub> system. © 2007 Elsevier B.V. All rights reserved.

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# 1. Introduction

Magnesium and magnesium-based compounds are natural candidate materials for solid state hydrogen storage. In fact, Mg is one of the least expensive and most abundant metals in the earth's crust; the theoretical hydrogen storage capacity of Mg (Mg + H<sub>2</sub>  $\rightarrow$  MgH<sub>2</sub>) is 8.3 wt% (7.6% if calculated with respect to MgH<sub>2</sub>), a value sufficient for commercial applications as a hydrogen fuel source [1–3]. While the Mg hydriding reaction is essentially reversible, its slow kinetics is a major problem; usually the magnesium powders must be "activated" by cycling several times from low to high hydrogen pressures at high temperature (more than 300 °C) before a reproducible absorption/desorption behavior is observed [4,5].

Preparation of Mg or  $MgH_2$  powders by high-energy ballmilling has been shown to be particularly effective in improving the sorption kinetics of the system down to few minutes at

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 $300 \,^{\circ}$ C. This may result from the high-surface area of the nanoparticles, from a high concentration of defects, which act as nucleation sites for the hydride phases and from crystallite boundaries, where fast hydrogen diffusion may occur [6–10]. However, the operational temperature is still too high for most applications. Addition of 3d transition metals should, on one hand, improve the absorption process by catalyzing H<sub>2</sub> dissociation and, on the other, increase the desorption rate by destabilizing the hydride phase.

By mechanically alloying Mg with transition metals, nanocrystalline Mg-based intermetallic compounds are obtained [11]. Some of them can directly react with hydrogen, forming a ternary Mg–M hydride; such a phase is generally less stable than MgH<sub>2</sub>, having a lower desorption temperature and a faster dehydrogenation kinetics. However, it also has a reduced hydrogen capacity compared with pure Mg. The best known example is given by the Mg–Ni system, first studied by Reilly and Wisall in 1968 [12] and, later, by many others [13–18]. Nanocrystalline Mg<sub>2</sub>Ni reacts fairly rapidly with hydrogen, to give Mg<sub>2</sub>NiH<sub>4</sub>, with a hydrogen intake of 3.6% and a desorption temperature of about 260 °C [19].

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Other Mg–M compounds do not form hydrides, but react readily with hydrogen when in nanocrystalline form, decomposing into MgH<sub>2</sub> and either an intermetallic phase or an alloy with a lower Mg content. This "nano-scale solid state reaction" [20] is reversible and the dissociation of MgH<sub>2</sub> takes place "driven" by the formation of a Mg-rich intermetallic compound. For example, it has been demonstrated that Mg<sub>2</sub>Cu nanopowders react with hydrogen at 300 °C, leading to the formation of MgH<sub>2</sub> and MgCu<sub>2</sub> [20,21] through a reaction which is almost fully reversible (the hydrogen uptake is 2.3wt%). Also aluminum has been found to destabilize MgH<sub>2</sub>; depending on the stoichiometry of the mixture [11,20], a Mg/Al solid solution or an intermetallic compound (Mg<sub>12</sub>Al<sub>17</sub>) is formed. At 280 °C, the equilibrium pressure of this system is three times larger than that of pure MgH<sub>2</sub>.

In this paper, nanocrystalline binary mixtures of Mg and nine different metals M (M = Al, Cu, Fe, Mo, Mn, Sn, Ti, Zn, Zr) have been prepared by mechanical alloying; their sorption capacities have been compared to study the effect of these additives as catalyzing/destabilizing agents for Mg hydrogenation/dehydrogenation. The evolution of the crystalline phases due to hydrogen absorption and subsequent desorption processes has been followed by X-ray powder diffraction analysis (XRPD) in mixtures with a M content as high as 63 wt%. Information on how the stoichiometry of the mixtures determine the kinetics of absorption/desorption and their mechanism, which may be relevant for the entire class of the Mg-based alloys, are also summarized.

#### 2. Experimental

#### 2.1. Materials

All Mg-based nanostructured mixtures were produced by MBN Nanomaterialia S.p.A (Vascon di Carbonera, Italy) by high-energy ball-milling process starting from commercially available metal powders. Mg (purity 99.5%, particle size 45–250  $\mu$ m), Cu (purity 99.7%, particle size 45–180  $\mu$ m), Sn (purity 99.7%, particle size <75  $\mu$ m) and Zn (purity 99.8%, particle size 45–150  $\mu$ m) were purchased from Pometon S.p.A; Mo (purity 99.5%, particle size 44–88  $\mu$ m), Mn (purity 99.7%, particle size <45  $\mu$ m), Fe (purity 99.5%, particle size 45–150  $\mu$ m) and Al (purity 99.4%, particle size 75–212  $\mu$ m) were purchased from Metalpolveri s.r.l.; Ti (purity 99.7%, particle size 1–4 mm) was supplied by MBN Nanomaterialia S.p.A.

For sake of simplicity, in all the text the binary mixtures will be written as  $Mg_xM_y$  (M = metal), with subscripts representing the weight percentage of every component.

## 2.2. Methods

#### 2.2.1. Samples preparation by ball-milling

MBN equipment consists of proprietary plant reactors [22] capable to process many hydrogen storage systems simultaneously. More than 100 g of nanostructured powders were produced per each batch. All systems were subjected to the same process conditions: high-energy milling with 10:1 ball to powder weight ratio under inert atmosphere (Ar) for 8 h at room temperature. After the process, nanopowders were discharged under Ar gas atmosphere in order to prevent any oxidative reaction and were put under a slight inert gas overpressure in stainless steel pressure-resistant containers designed and produced by MBN. Special lubricant-free valves are used in the containers to preserve the purity of the nanostructured systems. The powders were stored and handled in a glove box (Unilab MBraun, Germany) filled with purified and dry Ar ( $O_2$  and humidity contents <0.1 ppm).

#### 2.2.2. Samples activation and thermogravimetric analysis

The activation of the samples and the subsequent determination of their hydrogen storage properties were performed in a high-pressure thermogravimetric balance [Intelligent Gravimetric Analyzer IGA-001, Hiden Isochema, UK: capacity 5 g, weighing range 200 mg, mass resolution 0.2  $\mu$ g, long term stability (days)  $\pm 1 \mu$ g at room temperature and atmospheric pressure; pressure range  $10^{-6}$ -20 bar, temperature range 25–400 °C]. The hydrogen pressure variation rate was 200 mbar/min, while the temperature scan rate was  $10^{\circ}$ C/min. The typical sample mass was about 100 mg: with such a sample mass, the accuracy of the instrument (as determined by repeated measurements of a 100 mg standard weight) is  $\pm 50 \mu$ g ( $\pm 0.05\%$ ) and the precision of the measurements, determined over five identical hydrogenation/dehydrogenation runs, is  $\pm 0.1$  mg.

The powders were loaded into a quartz-wool covered Pyrex bulb with a diameter of 1 cm and then transferred from the glove box to the gravimetric apparatus under inert atmosphere using a stainless steel sample-loader (Hiden Isochema). The samples were kept at room temperature under vacuum for 15 min and then at 175 °C under 1 bar H<sub>2</sub> for 60 min in order to purify them from volatile substances. Before the analyses, all the samples were activated at 400 °C by cycling four times the hydrogen pressure  $PH_2$  from 1 to 20 bar, with isothermal/isobaric steps at the top and bottom pressure, respectively ("standard activation procedure", see Fig. 1). The isotherms/isobars at 400 °C/20 bar lasted 6 h during the first cycle and 2 h during the other three runs, while the steps at 400 °C/1 bar were always of 2 h. The total time needed for the activation was 29 h. A standard activation procedure is needed to improve the sorption properties of the milled materials and to obtain repeatable data for a meaningful comparison among mixtures. All the data presented hereafter refer to fully activated samples.

After the activation, the maximum hydrogen intake was determined at  $T_{\rm iso} = 370$  °C during a "standard charge procedure" consisting of two steps:

(a) increase of PH<sub>2</sub> from 1 to 20 bar;

(b) 6-h isobar at  $PH_2 = 20$  bar.

Subsequently, in order to gain information about the desorption process (minimum desorption temperature, kinetics, amount of released hydrogen),  $PH_2$  was decreased and kept constant to 1 bar, while the temperature was lowered to 250 °C, kept constant for 3 h and then raised in three subsequent isothermal steps, each lasting 3 h, at 300, 350 and 400 °C ("standard discharge procedure").

Finally, the standard charge and discharge procedures were performed a second time to assess the effect of both hydrogen pressure and temperature cycling on the sorption properties of the powders (cycle life, reversibility). The whole analysis lasted more than 48 h.



Fig. 1. Amount of absorbed/desorbed hydrogen (wt%, referred to the mass of the fully dehydrogenated sample: full line) and hydrogen pressure (dashed line) profiles recorded at 400 °C during the activation standard procedure for  $Mg_{70}Fe_{30}$ .

In the following, the amount of hydrogen absorbed/desorbed by the mixtures during the charge–discharge procedures will be expressed in wt%. The data are calculated by relating the mass values recorded by the instrument in real time with the "dry-mass" of the sample, i.e. the mass of the fully dehydrogenated sample. The average absorption/desorption speed values (wt% total H<sub>2</sub> intake/min) are obtained as the ratio between the total amount of charged/released hydrogen (wt%) and the time (min) needed for the completion of the process.

## 2.2.3. Samples characterization

X-ray powder diffraction analyses (XRPD) were performed under Ar flux with a Bruker D5005 diffractometer ( $2\theta = 15-85^\circ$ , Cu K $\alpha$  radiation, step scan mode, step width 0.014°, counting time 1 s, 40 kV, 30 mA; PSD detector).

The powders were dispersed on a Si slide under Ar atmosphere in the glove box, and then covered with a thin plastic film (with no diffraction peaks in the angular range considered in this work), in order to avoid contamination or Mg oxidation. No MgO peaks have ever been detected in the diffraction patterns. The samples were examined before and after the charge and the discharge procedures.

After XRPD analysis, all the samples containing hydride phases (both the "fully charged" samples and those with a partially reversible sorption) were put in an alumina crucible and subjected to a 2 h thermal treatment at 400 °C in a tubular oven (Elite, Italy) under Ar atmosphere (the tubular oven was placed in the glove box). This treatment in nominally zero hydrogen pressure is believed to achieve full dehydrogenation.



Fig. 2. SEM micrographs at low and high magnifications of  $Mg_{43}Cu_{57}$  powders as-milled (a, b), after two charge–discharge cycles (c, d) and after the standard charge procedure (e, f) and of  $Mg_{70}Fe_{30}$  powders after the standard charge procedure (g, h).



Fig. 2. (Continued).

Sample micrographs have been collected with a scanning electron microscope (SEM) Cambridge Stereoscan 200 (UK) on gold sputtered samples.

# 3. Results and discussion

# 3.1. SEM analysis

In all the mixtures, the milling process leads to the formation of aggregates (Fig. 2a) of very different sizes, from 30 to 120  $\mu$ m, which in turn have surfaces covered with grains as small as 0.5–5  $\mu$ m (Fig. 2b). The combined temperature/hydrogen pressure treatments leads to no meaningful changes in the average dimensions of the particles and both the morphology and the microstructure of the powders after dehydrogenation (Fig. 2c and d) are the same as the as-milled powders. This is in agreement with the findings of Zaluska et al. [20] and explains why the hydrogenation performances of the magnesium-based systems are maintained over many cycles of hydrogenation/dehydrogenation.

In the "fully hydrogenated samples" belonging to Mg–Cu, Mg–Al and Mg–Zn systems the powders grains (Fig. 2e) are constituted by homogenous nanoparticles aggregates (Fig. 2f) with a characteristic "rounded" nanostructure (typical of thermal treated MgH<sub>2</sub>) and average size as low as 100–200 nm. For the other systems, the appearance of the charged samples is less homogenous (Fig. 2g), with the little rounded hydride particles lying on unreacted squared and larger metal grains (Fig. 2h).

# 3.2. Charge-discharge steps

Fig. 3 reports the amount of hydrogen (wt%) absorbed/desorbed during two subsequent charge/discharge cycles (see the pressure and temperature profiles) by  $M_{g70}Cu_{30}$  (a),  $Mg_{46}Fe_{54}$  (b),  $Mg_{70}Al_{30}$  (c), and  $Mg_{70}Zr_{30}$  (d), i.e. four samples with substantially different hydrogenation behaviors.

For all the mixtures, the absorption process begins as  $PH_2$  is increasing to 20 bar and the absorption/desorption profiles are very similar during the two cycles: these observations point out that the activation procedure has been successful to improve Mg sorption kinetics. Sorption always begins at the equilibrium pressure of the sample ( $P_{eq,min}$ ): such a pressure ranges between 5 and 10 bar depending on chemical composition and, as shown below, on stoichiometry. There is a quick linear kinetics up to 15–18 bar, suggesting that in our experimental conditions the sorption process is driven by the pressure scanning rate.  $Mg_{70}Cu_{30}$  and  $Mg_{70}Al_{30}$  (Fig. 3a and c) absorb more than 80% of the overall hydrogen intake during this linear step, with an average absorption speed of  $8 \times 10^{-2}$  wt% H<sub>2</sub>/min. During the isobaric/isothermal stage the absorption process takes place with a much slower kinetics ( $2 \times 10^{-3}$  wt% H<sub>2</sub>/min) till the equilibrium hydrogen content is reached. On the other hand, the amount of hydrogen stored by  $Mg_{46}Fe_{54}$  (Fig. 3b) and  $Mg_{70}Zr_{30}$ (Fig. 3d) during the pressure increase is as low as 68% and 47% of the overall intake, and the hydrogen content of these mixtures is still rising significantly after the 6 h isobar/isothermal step.

Concerning the discharge process ( $PH_2$  fixed at 1 bar), we will call "minimum desorption temperature" ( $T_{min}$ ) the lowest temperature at which the sample starts to release hydrogen with an average speed higher than  $10^{-3}$  wt% of the total  $H_2$  intake/min. Generally, the desorption process is characterized by a quick linear kinetics already at the minimum desorption temperature and an additional increase of temperature causes an even faster hydrogen release (Fig. 3a).

As evident from Fig. 3, for both the cycles the amount of hydrogen released during the discharge step is generally slightly lower than the intake recorded during the correspondent charge step (0.1–0.3 wt% H<sub>2</sub>, depending upon chemical composition), i.e. the cycles are not fully reversible: as discussed below, at T = 400 °C the desorption process needs a hydrogen pressure lower than 1 bar to be completed. Moreover, for all the samples the amounts of hydrogen absorbed/desorbed during the 2nd cycle are lower than the correspondent values of the 1st cycle. This means that there is a worsening of the sorption capacity of the mixtures due to temperature/hydrogen pressure cycling.

In the following, with the aim to estimate reversibility and worsening due to cycling, we will say that a hydrogenation cycle is "reversible" if the sample discharges at least 90% of the absorbed hydrogen. We will also say that a "cycling effect" is present if the second full charge/discharge cycle after activa-



Fig. 3. Amount of absorbed/desorbed hydrogen (wt%, full line), temperature (dashed-dotted line) and hydrogen pressure (dashed line) profiles recorded during two charge–discharge cycles for  $Mg_{70}Cu_{30}$  (a),  $Mg_{46}Fe_{54}$  (b),  $Mg_{70}Al_{30}$  (c), and  $Mg_{70}Zr_{30}$  (d).

tion involves less than 95% of the hydrogen amount of the first cycle. According to these cut-off criteria:- Mg70Cu30 (Fig. 3a) is characterized by reversible hydrogenation and no cycling effect (it absorbs/desorbs during the 2nd cycle exactly the same amount of H<sub>2</sub> involved during the 1st one);  $-Mg_{46}Fe_{54}$  (Fig. 3b) shows reversible cycles and no cycling effect even if it just falls within the cut-off limits regarding both the characteristics (in both the cycles it desorbs 91% of the hydrogen intake and the second cycle involves exactly 95% of the hydrogen amount of the first cycle);  $-Mg_{70}Al_{30}$  (Fig. 3c) gives reversible reactions (even 100% in the 1st run and 97% in the 2nd one) but shows a strong cycling effect (the 2nd cycle involves less than 85% the hydrogen amount of the 1st one);  $-Mg_{70}Zr_{30}$  (Fig. 3d) suffers from both no reversibility (only 82% of the "H<sub>2</sub> charge" is desorbed in both the runs) and strong cycling effect (the amount of H<sub>2</sub> exchanged during the 2nd cycle is only 65% of the 1st run).

During cooling to room temperature ( $PH_2 = 1$  bar) following the discharge step, an absorption process takes place beginning around T = 270 °C and ending around 220 °C (right part of Fig. 3b and d) in all the mixtures containing "free" Mg (see below). The average speed of this process is similar to the one recorded when the absorption is "driven" by the hydrogen pressure increase at 370 °C and in some cases leads to an H<sub>2</sub> intake up to 40–50% of the total amount stored after the charge step (see Fig. 3b). Such a behavior can be explained by taking into account that the hydrogen equilibrium pressure of the system Mg/MgH<sub>2</sub> at 275 °C is 1 bar [19]: when  $PH_2 = 1$  bar (as during cooling of our samples) and the temperature falls below 275 °C but remains sufficiently high to sustain the kinetics of the gas–solid reaction, we can have H<sub>2</sub> absorption as a consequence of MgH<sub>2</sub> formation.

# 3.3. Mg–M binary systems

## 3.3.1. Sorption capacities

Table 1 reports the sorption capacities recorded for the binary Mg–M mixtures.

Mixtures with composition  $Mg_{70}M_{30}$  (listed in italic in the table) have been prepared for all the systems for sake of comparison. For five systems, also mixtures with different compositions have been prepared [namely: (a) for the Mg–Cu, Mg–Al and Mg–Zn systems, mixtures with molar ratio close to the stoichiometry of the intermetallic compounds present in the binary phase diagrams (see below); (b) for the Mg–Fe system, samples with a Mg:Fe molar ratio  $\approx 2:1$ , as in the ternary hydride Mg<sub>2</sub>FeH<sub>6</sub>; (c) for the Mg–Ti system, mixtures with a 10 wt% lower Ti content, to assess if a little variation in the relative amounts of the two metals, both hydrogen absorbing species, could affect the storage properties].

For the  $Mg_{70}M_{30}$  samples the theoretical maximum hydrogen intake, calculated in the hypothesis that Mg quantitatively reacts with hydrogen forming MgH<sub>2</sub>, is 5.8 wt%. Table 1 shows that  $Mg_{70}Cu_{30}$  is the best performing mixture, showing the highest hydrogen intake  $H_{2,tot}$  (5.1 wt%, reasonably close to the theoretical value) combined with good reversibility and no cycling effect (at least, in the first two cycles). However, the minimum desorption temperature of this system is 320 °C, a value comparable with that of dissociation of pure MgH<sub>2</sub> and hence too high for practical applications.

The addition of other metals to Mg leads to a worsening of its performances as hydrogen storage medium: the hydrogen intakes fall well below the theoretical value, dropping to  $\approx 2\%$  when M = Sn and Zr. With the exceptions of M = Mn and Zn, the

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Table 1 Sorption properties of the binary systems Mg–M in the framework of the two performed charge–discharge cycles (see text)

Composition (weight %)	1st cycle			2nd cycle		R	C	
	P <sub>eq,min</sub> (bar)	abs. H <sub>2</sub> ( $H_{2,tot}$ , wt%)	$T_{\min}$ (°C)	des. H2 (wt%)	abs. H <sub>2</sub> (wt%)	des. H2 (wt%)		
Mg 70% + Cu 30%	5	+5.1	320	-5.0	+5.0	-4.9	Y	N
Mg 43% + Cu 57%	10	+2.4	270	-2.2	+2.3	-2.2	Y	Ν
Mg 70% + Zn 30%	8	+4.5	360	-4.2	+4.3	-4.0	Y	Ν
Mg 50% + Zn 50%	11	+2.8	340	-2.7	+2.4	-2.3	Y	Y
Mg 70% + Al 30%	8	+4.3	320	-4.3	+3.6	-3.5	Y	Y
Mg 55% + Al 45%	10	+3.8	340	-2.8	N.R.	N.R.	Ν	_
Mg 37% + Al 63%	11	+1.3	350	-0.7	N.R.	N.R.	Ν	_
Mg 80% + Ti 20%	8	+3.3	320	-3.2	+3.2	-3.1	Y	Ν
Mg 70% + Ti 30%	9	+3.3	320	-2.7	+2.9	-2.5	Ν	Y
Mg 70% + Fe 30%	6	+3.1	320	-2.6	+2.8	-2.2	Ν	Y
Mg 46% + Fe 54%	7	+2.1	315	-2.0	+2.0	-1.9	Y	Ν
Mg 70% + Mo 30%	9	+3.4	370	-3.2	+3.0	-2.8	Y	Y
Mg 70% + Mn 30%	9	+2.9	320	-2.9	+2.9	-2.9	Y	Ν
Mg 70% + Sn 30%	6	+2.3	400	-2.1	+2.1	-1.8	Ν	Y
Mg 70% + Zr 30%	6.5	+1.7	340	-1.4	+1.1	-0.9	Ν	Y

In italic, the  $Mg_{70}M_{30}$  mixtures.  $P_{eq,min}$ : equilibrium pressure of the sample at 370 °C and minimum pressure value where absorption begins.  $T_{min}$ : minimum desorption temperature (H<sub>2</sub> pressure fixed at 1 bar). R: reversibility: the absorption/desorption process is reversible if the sample discharges at least 90% of the absorbed hydrogen. C: cycling effect: the sample shows cycling effect if the second full charge/discharge cycle after activation involves less than 95% of the hydrogen amount of the first cycle. Y: yes; N: no; N.R.: not recorded.

 $Mg_{70}M_{30}$  mixtures suffer from "cycling effects". Furthermore, for the mixtures containing Fe, Ti, Sn and Zr the reversibility of the sorption process is lower than 90% (i.e. our cut-off limit) at  $PH_2 = 1$  bar and temperatures in the range 250–400 °C (the values characterizing the discharge step). Even though these mixtures still contain hydrogen after the discharge procedure at 1 bar, they can be fully dehydrogenated with a 2 h thermal treatment at 400 °C in Ar atmosphere (i.e., with a hydrogen pressure very close to zero).

The minimum desorption temperatures recorded in the presence of all these additives are generally higher than that of pure MgH<sub>2</sub>:  $T_{min}$  is 360–370 °C for  $Mg_{70}Zn_{30}$  and  $Mg_{70}Mo_{30}$  and even 400 °C for  $Mg_{70}Sn_{30}$ . In short, these metals do not act as MgH<sub>2</sub> destabilizing agents.

When the Mg:M ratio is decreased, the maximum  $H_2$  intake always drops: a decrease in the Mg content (wt%) from 70% to values near 40% leads to a reduction in the  $H_2$  intake (wt%) of 1.5 times for the Mg–Fe system, of 2.1 times in the case of the Mg–Cu system and of more than three times for the Mg–Al mixtures.

 $P_{eq,min}$  increases with M content for all the systems. The strongest variation is recorded when M=Cu ( $P_{eq,min}$  doubles when the Cu amount is increased from 30% to 57%). The highest  $P_{eq,min}$  values are recorded for the Cu, Al and Zn-richest mixtures.

As it concerns the minimum desorption temperature:

- (i) it decreases significantly ( $\approx 10^{\circ}$ C) with the Mg content in the presence of Cu and Zn;
- (ii) it decreases in a lower extent in the Mg–Fe system (only 5°C for a Mg decrease of even 24 wt%);
- (iii) it does not change for a Mg content decrease of 10% in the Mg-Ti system;

(iv) it increases slightly with decreasing Mg content from 70% to 55% and finally to 37% in the Mg–Al mixtures.

Last but not least, the decrease of Mg content affects the reversibility of all but two Mg–M systems. The unaffected mixtures are those containing Cu (which perform very well also for low-Mg contents) and Zn. The performances change from reversible to non-reversible for M = Al and Ti, while the opposite happens for M = Fe.

## 3.3.2. Hydrogenation/dehydrogenation mechanism

The fact that a decrease in the Mg content consistently causes a decrease in the H<sub>2</sub> intake in all the systems suggests that magnesium is the most efficient or the only hydrogen absorbing species. The XRPD analyses performed on the samples after mechanical milling and following the different steps of the sorption processes (Table 2) gives evidence of this key-point. With the only exception of the mixtures containing Ti,<sup>1</sup> our data show that the only hydride phase in all the charged samples is MgH<sub>2</sub>: this means that Mg is the only hydrogen absorbing species.

From the binary phase diagrams [24], we know that Mg can form one intermetallic compound with Sn, two with Cu and several with Al and Zn. As evident from Table 2, milling causes formation of one intermetallic compound in all the mixtures containing these four metals (with the only exception of the  $Mg_{50}Zn_{50}$  case discussed below). Such a compound is generally the richest in Mg among the ones in the phase diagrams (with the exception of  $Mg_{70}Zn_{30}$  and  $Mg_{37}Al_{63}$ ) and is present also in the "discharged sample". On the other hand, an intermetallic compound with lower Mg content is always present,

 $<sup>^{1}</sup>$  In these samples also the two hydrides TiH<sub>1.924</sub> (in agreement with the findings of Grigorova et al. [23]) and TiH<sub>1.971</sub> form upon hydrogenation.

Table 2

Composition (wt%)	As-prepared sample	Charged sample	Discharged sample	
Mg 70% + Cu 30%	$Mg(+), Mg_2Cu(\approx)$	$MgH_2$ (+), $MgCu_2$ ( $\approx$ ), $Mg_2Cu$ (t)	$Mg(+), Mg_2Cu(\approx)$	
Mg 43% + Cu 57%	Mg <sub>2</sub> Cu	MgH <sub>2</sub> (+), MgCu <sub>2</sub> ( $\approx$ )	$Mg_2Cu$ (+), $MgCu_2$ (t)	
Mg 70% + Zn 30%	$Mg(+), Mg_4Zn_7(t)$	$M_{g}H_{2}(+), M_{g}(\approx), M_{g}Z_{n_{7}}(\approx)$	$Mg(+), Mg_4Zn_7(\approx)$	
Mg 50% + Zn 50%	Mg (+), amorphous Zn (t)	MgH <sub>2</sub> (+), MgZn <sub>2</sub> ( $\approx$ )	Mg <sub>7</sub> Zn <sub>3</sub>	
Mg 70% + Al 30%	$Mg(+), Mg_{17}Al_{12} (\approx)$	$M_{g}H_{2}(+), M_{g_{2}}Al_{3}(\approx), M_{g_{17}}Al_{12}(t)$	$Mg(+), Mg_{17}Al_{12} (\approx)$	
Mg 55% + Al 45%	$Mg_{17}Al_{12}$	$MgH_2$ (+), $Mg_2Al_3$ ( $\approx$ ), $Al$ ( $\approx$ ), $Mg_{17}Al_{12}$ (t)	$Mg_{17}Al_{12}$ (+), $Mg_2Al_3$ ( $\approx$ )	
Mg 37% + Al 63%	Amorphous phases (Mg <sub>2</sub> Al <sub>3</sub> ?)	$Mg_2Al_3$ (+), $MgH_2$ ( $\approx$ ), $Mg_{17}Al_{12}$ (t), Al (t)	$Mg_2Al_3$ (+), $Mg_{17}Al_{12}$ (t)	
Mg 80% + Ti 20%	Mg (+), Ti (≈)	Mg (+), MgH <sub>2</sub> ( $\approx$ ), TiH <sub>1.924</sub> ( $\approx$ ), TiH <sub>1.971</sub> ( $\approx$ )	Mg (+), Ti (≈)	
Mg 70% + Ti 30%	$Mg(+), Ti(\approx)$	$Mg(+), MgH_2(\approx), TiH_{1.924}(\approx), TiH_{1.971}(\approx)$	$Mg(+), Ti(\approx)$	
Mg 70% + Fe 30%	$Mg(+), Fe(\approx)$	$MgH_2(+), Fe(\approx), Mg(\approx)$	$Mg(+), Fe(\approx)$	
Mg 46% + Fe 54%	Mg (+), Fe ( $\approx$ )	$MgH_2$ (+), Fe ( $\approx$ ), $Mg$ ( $\approx$ )	Mg (+), Fe ( $\approx$ )	
Mg 70% + Mo 30%	$Mg(+), Mo(\approx)$	$M_{g}H_{2}(+), M_{O}(\approx), M_{g}(\approx)$	$Mg(+), Mo(\approx)$	
Mg 70% + Mn 30%	$Mg(+), Mn(\approx)$	$M_{g}H_{2}(+), Mn(\approx), Mg(\approx)$	$Mg(+), Mn(\approx)$	
Mg 70% + Sn 30%	$Mg(+), Mg_2Sn(\approx)$	$Mg_2Sn \ (\approx), MgH_2 \ (\approx), Mg \ (\approx)$	$Mg(+), Mg_2Sn(\approx)$	
Mg 70% + Zr 30%	Mg(+), amorphous $Zr(t)$	$MgH_2(+), Zr(\approx), Mg(\approx)$	$Mg(+), Zr(\approx)$	

Results of XRPD analysis performed on the Mg-M binary mixtures as-milled ("as-prepared sample"), after the first charge step ("charged sample"), and after two complete charge-discharge cycles followed by thermal treatment in Ar at 400 °C to achieve full dehydrogenation ("discharged sample")

In italic, the  $Mg_{70}M_{30}$  mixtures. (+): most conspicuous phase, ( $\approx$ ): intermediate amount, (t): traces.

together with MgH<sub>2</sub>, in the charged samples. This suggests that the Mg-rich compound acts as "Mg reserve" and upon hydrogenation/dehydrogenation gives rise to a "Mg exchange" with the compound of low-Mg content. This mechanism provides both "free" Mg to react with H<sub>2</sub> during the charge step and an intermetallic compound, which "destabilizes" MgH<sub>2</sub> during the discharge step.

3.3.2.1. Mg-Cu system. In both the mixtures of this system, milling leads to the formation of the Mg-richest phase Mg<sub>2</sub>Cu. Upon hydrogenation/dehydrogenation, an exchange takes place between this phase and MgCu<sub>2</sub>, the other intermetallic compound of the Mg-Cu system. The likely reaction [11,20,21] is:

$$2Mg_2Cu + 3H_2 \rightleftharpoons 3MgH_2 + MgCu_2 \tag{1}$$

It is interesting to note (Table 1) that for  $Mg_{43}Cu_{57}$ : (a) the desorption temperature at  $P H_2 = 1$  bar is 270 °C, i.e. 50 °C lower than the desorption temperature of Mg and  $Mg_{70}Cu_{30}$ ; (b)  $P_{\rm eq,min}$  at 370 °C is 10 bar, i.e. double than the value recorded for  $Mg_{70}Cu_{30}$ . A possible explanation of such differences is that in  $Mg_{43}Cu_{57}$  the molar amounts of Mg and Cu are just enough to form Mg<sub>2</sub>Cu and hydrogenation/dehydrogenation takes place according to (1), where MgCu<sub>2</sub> acts as a destabilizing agent for MgH<sub>2</sub>. On the other hand, in  $Mg_{70}Cu_{30}$  there is a considerable amount of excess or "free" Mg and the low amount of MgCu<sub>2</sub> formed from Mg<sub>2</sub>Cu upon hydrogenation is not effective as destabilizing agent for MgH<sub>2</sub>. The presence of two different sorption mechanisms in this Mg-rich mixture is confirmed by the presence of two absorption steps during the standard charge procedure (pressure sweep to  $PH_2 = 20$  bar at 370 °C, see Fig. 3a): the 1st step, starting at 5 bar, is attributable to "free Mg" hydrogenation, while the second one, starting at about 14.5 bar, is due to reaction (1).

It must be highlighted that the  $T_{des}$  value recorded for  $Mg_{43}Cu_{57}$  is very close to the experimental values quoted in literature as the minimum temperature needed to obtain full dehydrogenation at  $PH_2 = 1$  bar with good kinetics (280-300°C [25,21]). Really, from the thermodynamic data reported in literature for reaction (1) ( $\Delta H = -77$  to  $-70 \text{ kJ/mol}, \Delta S \approx -145 \text{ J/mol} \text{ H}_2 \text{ [21,26-28]}, T_{\text{des}} \text{ values as}$ low as 210-255 °C could be expected (calculated through the van't Hoff equation). In the same time,  $P_{eq,min}$  as high as 24-30 bar could be expected, to be compared with our 10 bar experimental value. This means that the destabilizing effect of MgCu<sub>2</sub> towards MgH<sub>2</sub> is not yet fully deployed, probably due to kinetics barriers. Anyway, an improvement in the desorption kinetics performances with respect to the pure Mg/MgH<sub>2</sub> system is evident: desorption in Mg43Cu57 takes place much faster and at lower temperature than in 15 h ball-milled MgH\_2 powders (13  $\times$  10^{-2} wt% H\_2/min at 270  $^{\circ}C$ and  $PH_2 = 1$  bar vs.  $1.3 \times 10^{-2}$  wt% H<sub>2</sub>/min at 300 °C and  $PH_2 = 10 \text{ mbar } [29]).$ 

3.3.2.2. Mg-Al system. For this system, two different reaction mechanisms appear to be present: this offers the possibility to tailor the sorption properties of the samples by varying their Al content [20]. The two intermetallic phases involved in the sorption mechanism are Mg<sub>17</sub>Al<sub>12</sub> and Mg<sub>2</sub>Al<sub>3</sub> (Table 2).

Milling produces the Mg-richest phase in both  $Mg_{70}Al_{30}$  and  $Mg_{55}Al_{45}$ . The XRPD patterns of as-milled  $Mg_{37}Al_{63}$ , with only a large and unidentified peak, point to the presence of amorphous phases. Since our milling procedure does not lead to amorphization of Mg, it is likely that, in this case, all magnesium has reacted with Al to form amorphous Mg<sub>2</sub>Al<sub>3</sub>. In fact, the crystalline counterpart of this phase is identified in the XRPD pattern taken after 1 h treatment of the milled mixture at 400 °C in Argon.

In  $Mg_{70}Al_{30}$ , there is an excess of Mg over the stoichiometry of both intermetallic compounds and the hydrogenation reaction appears to follow the scheme

$$Mg_{17}Al_{12} + 9H_2 \rightleftharpoons 9MgH_2 + 4Mg_2Al_3 \tag{2}$$

The hydrogen absorbed during the pressure increase is about 80% of the total intake; the average absorption rate is

 $8 \times 10^{-2}$  wt% H<sub>2</sub>/min, comparable with that of  $Mg_{70}Cu_{30}$ . Desorption begins at the same  $T_{min}$  (320 °C) in the two  $Mg_{70}M_{30}$  mixtures, but it is more than three times slower when M = Al (3 × 10<sup>-2</sup> wt% H<sub>2</sub>/min vs. 1 × 10<sup>-1</sup> wt%/min).

In  $Mg_{55}Al_{45}$  and  $Mg_{37}Al_{63}$  (mixtures with a Mg:Al ratio lower than 17:12), both Al and Mg<sub>2</sub>Al<sub>3</sub> are formed during the charge step:

$$Mg_{17}Al_{12} + 11H_2 \rightleftharpoons 11MgH_2 + 3Mg_2Al_3 + 3Al$$
(3)

The hydrogenation/dehydrogenation rates of this reaction are lower than those of reaction (2), and decrease with decreasing the Mg content. In  $Mg_{55}Al_{45}$  the hydrogen absorption during the pressure increase step is just 66% of the total intake and both absorption and desorption take place at rates of the order of  $3 \times 10^{-2}$  wt% H<sub>2</sub>/min. In  $Mg_{37}Al_{63}$  the hydrogen intake during the pressure increase step is only 10% of the total amount, the absorption rate is  $3 \times 10^{-3}$  wt% H<sub>2</sub>/min and the desorption rate is  $1 \times 10^{-3}$  wt% H<sub>2</sub>/min, i.e. about one order of magnitude less than in  $Mg_{55}Al_{45}$ . The desorption temperature is above 340 °C for both the mixtures.

The reaction scheme generally reported in literature for Mg–Al systems is [20,30,31]:

$$Mg_nAl_m + nH_2 \rightleftharpoons nMgH_2 + mAl$$
 (4)

where the entire amount of Mg present in  $Mg_nAl_m$  reacts with hydrogen during charge, leading to the formation of MgH<sub>2</sub> and Al. The full dissociation of the Mg–Al intermetallic during hydrogenation is explained by the lower stability of this compound if compared to that of MgH<sub>2</sub> [31]. The composition of the Mg–Al phase present in the dehydrogenated state depends on the relative concentration of Mg and Al in the starting mixtures and this results in differences in the thermodynamic characteristics of the systems, but the equilibrium pressures recorded for reaction (4) are always shifted to higher value than pure Mg/MgH<sub>2</sub> system. This points out the good destabilizing effect exerted by Al vs. MgH<sub>2</sub>.

On the contrary, in our mixtures also a Mg-Al phase (i.e. Mg<sub>2</sub>Al<sub>3</sub>) forms upon charge, due to the incomplete hydrogenation of Mg<sub>17</sub>Al<sub>12</sub>, as observed also by other authors in Refs. [32,33]. This means that in our samples Mg<sub>17</sub>Al<sub>12</sub> is more stable than expected towards the hydrogenation process. From the few plateau pressure data reported in literature for reaction (4) (only one value for  $Mg_nAl_m = Mg_{17}Al_{12}$  [20], two sets of data for  $Mg_nAl_m = Mg_2Al_3$  [30,31]) the van't Hoff plot allows to obtain for reaction (4) average values of  $\Delta H \approx -62.7$  kJ/mol and  $\Delta S \approx -124$  J/mol [34]. From these values, a desorption temperature as low as 234 °C at  $PH_2 = 1$  bar and a  $P_{eq,min} \approx 24$  bar at 370 °C could be expected if Mg full hydrogenation/dehydrogenation takes place according to Eq. (4). The values quoted above are very different from those reported in Table 1 for reactions (2) and (3) (namely, the desorption temperature is about 100°C lower and the pressure is 14 bar higher than our experimental values), pointing out that in our mixtures neither Mg<sub>2</sub>Al<sub>3</sub> nor  $Mg_2Al_3 + Al$  are able to exert an appreciable destabilizing effect vs. MgH<sub>2</sub>.

3.3.2.3. Mg–Zn system. In  $Mg_{50}Zn_{50}$  milling is not so effective to induce a reaction between Mg and Zn (however, a Mg-rich intermetallic phase, Mg<sub>7</sub>Zn<sub>3</sub>, is produced by annealing in Ar at 400 °C the milled sample). The charged sample contains MgZn<sub>2</sub> together with the hydride MgH<sub>2</sub> (according to [35]), while only the phase Mg<sub>7</sub>Zn<sub>3</sub> is present in the discharged sample (after two full charge/discharge cycles). This suggests that the hydrogenation/dehydrogenation reaction taking place in this mixture is

$$2Mg_7Zn_3 + 11H_2 \rightleftharpoons 11MgH_2 + 3MgZn_2 \tag{5}$$

This reaction takes place with rates much lower than those of the Mg–Cu system  $(2 \times 10^{-2} \text{ wt\% H}_2/\text{min})$  in absorption and  $3 \times 10^{-2} \text{ wt\% H}_2/\text{min}$  in desorption). The hydrogen fraction absorbed during pressure increase is 60% of the total intake. The above suggests that the reactions involving intermetallic phases in this system are kinetically limited: this could be the reason why milling does not induce a Mg–Zn reaction and the subsequent formation of an intermetallic phase.

In  $Mg_{70}Zn_{30}$ , both as-milled and discharged, most Zn is present as Mg<sub>4</sub>Zn<sub>7</sub>, phase which appears to be quite stable, and unable to react with hydrogen. The improved hydrogen intake (4.5%) and kinetic performances (absorption rate:  $5 \times 10^{-2}$  wt% H<sub>2</sub>/min, desorption rate  $4 \times 10^{-2}$  wt% H<sub>2</sub>/min) of this mixture with respect to  $Mg_{50}Zn_{50}$  are due to the presence of a large amount of "free" Mg and to the fact that no intermetallic phase takes active part in Mg hydrogenation/dehydrogenation.

To our knowledge, few studies in literature are devoted to the clarification of the hydrogenation/dehydrogenation mechanism in Mg–Zn mixtures [35–37] and neither thermodynamic data nor equilibrium plateau pressure results are available for a meaningful comparison with our thermogravimetric desorption results.

3.3.2.4. Mg–Sn system. According to the phase diagram [24], Mg and Sn form only the intermetallic compound Mg<sub>2</sub>Sn. Such a compound is present in similar amounts in  $Mg_{70}Sn_{30}$  both before charge and after discharge: this suggests that is not involved in the Mg hydrogenation/dehydrogenation reaction and only acts as "Mg trap", reducing the content of this element in the mixture and hence its hydrogen storage capacity. Furthermore, some unreacted Mg is present, together with MgH<sub>2</sub>, in the charged sample, meaning that the formation of the intermetallic limits somehow the fully hydrogenation of Mg; it is likely that the presence of Mg<sub>2</sub>Sn is also the cause of the sluggish kinetics of the mixture (absorption rate:  $2 \times 10^{-2}$  wt% H<sub>2</sub>/min, desorption rate  $4 \times 10^{-3}$  wt% H<sub>2</sub>/min).

3.3.2.5. Other Mg–M systems. Fe, Mn, Mo, and Zr do not form binary compounds with Mg [24]; the characteristic reflections of these metals are present, with comparable intensities, in the patterns of the as-milled mixtures (Table 2) and of the charged and discharged samples. We would expect that the entire Mg amount of the mixture could be free to react with hydrogen, leading to the formation of MgH<sub>2</sub> and hence to intakes close to the theoretical maximum value, i.e. 5.8 wt% for the  $Mg_{70}M_{30}$  mixtures.

Table 3
Sorption performances of the binary Mg-M systems

Composition (wt%)	<i>H</i> <sub>2,tot</sub> (wt%)	<i>H</i> <sub>2,th</sub> (wt%)	$H_{2,\text{last h}}$ (wt%)	$(H_{2,\text{last h}}/H_{2,\text{tot}}) \times 100$	Sorption efficiency
Mg 70% + Cu 30%	+5.1	+5.3	+0.04	0.78	96
Mg 43% + Cu 57%	+2.4	+2.7	+0.02	0.80	88
Mg 70% + Zn 30%	+4.5	+5.3	+0.05	1.11	85
Mg 50% + Zn 50%	+2.9	+5.0	+0.11	3.79	58
Mg 70% + Al 30%	+4.3	+4.3	+0.11	2.62	100
Mg 55% + Al 45%	+3.8	+4.2	+0.10	2.68	90
Mg 37% + Al 63%	+1.3	+1.5	+0.08	6.15	87
Mg 80% + Ti 20%	+3.3	+7.5	+0.10	2.78	44
Mg 70% + Ti 30%	+3.3	+7.2	+0.14	4.24	46
Mg 70% + Fe 30%	+3.1	+5.8	+0.06	1.71	53
Mg 46% + Fe 54%	+2.1	+3.8	+0.07	2.92	55
Mg 70% + Mo 30%	+3.4	+5.8	+0.09	2.65	59
Mg 70% + Mn 30%	+2.9	+5.8	+0.13	2.95	50
Mg 70% + Sn 30%	+2.3	+4.8	+0.09	3.91	48
Mg 70% + Zr 30%	+1.7	+5.8	+0.15	8.33	29

In italic, the  $Mg_{70}M_{30}$  mixtures.  $H_{2,tot}$ : total H<sub>2</sub> intake (wt%) recorded during the 6 h isothermal/isobaric charge step at 370 °C and 1 bar H<sub>2</sub> (1st cycle).  $H_{2,th}$ : theoretical H<sub>2</sub> intake (wt%) calculated in accordance with the hydrogenation/dehydrogenation mechanisms described in the text.  $H_{2,last h}$ : H<sub>2</sub> intake (wt%) recorded during the last hour of the isothermal/isobaric charge step at 370 °C and 1 bar H<sub>2</sub> (1st cycle). Sorption efficiency:  $H_{2,tot}/H_{2,th} \times 100$ . In bold the mixtures characterized by a *not complete absorption process*; i.e. ( $H_{2,last h}/H_{2,tot}$ ) × 100 > 3 (empirical threshold).

However, in all the "charged" samples some unreacted Mg is present and the hydrogen storage capacities of these systems are much lower than expected. A much lower than expected storage capacity (see Table 1) is also shown by the Ti containing mixtures, even if (unlike the other metals quoted in this paragraph) Ti acts as "hydriding element" and Ti hydrides form, together with MgH<sub>2</sub>, during the charge step.

All the five metals, when present in the substantial molar fractions considered here, strongly hinder the reaction between Mg and H<sub>2</sub>. Maybe the milling process leads to the formation of Mg–M agglomerates where sites for H<sub>2</sub> dissociation and absorption on Mg surface are shielded by M. This description qualitatively agrees with the kinetics data: for all the mixtures containing these additives, the amount of hydrogen absorbed during the pressure increase step is less than 60% of the total intake and the average absorption and desorption rates are all in the 2–4 × 10<sup>-2</sup> wt% H<sub>2</sub>/min range, i.e. values comparable with those of reactions (2), (3), (5) but much lower than those of Mg–Cu mixtures [reaction (1)] and pure Mg [25].

#### 3.3.3. Sorption efficiency

As discussed above, when Fe, Mn, Mo, Zr are added to Mg, no intermetallic compound is formed and some Mg does not react with hydrogen: the hydrogen storage capacity of the mixture is only due to the "reactive part of its free Mg content" (which is lower than the nominal Mg content) since none of these metals reacts with H<sub>2</sub>. On the other hand, when Mg is mixed with Al, Cu, Sn and Zn, intermetallic compounds are formed. However, such compounds are not able to give intermetallic hydrides: they only trap some Mg with the result that the hydrogen storage capacity of the mixture is due to its "reactive Mg content" (which is again lower than the nominal content but for these systems is constituted by the entire amount of free Mg and part of bounded Mg).

As we know the stoichiometry of the mixtures and of the intermetallic phases present both in the charged and discharged

samples, we may compute in all cases the "reactive" Mg content of the mixture and therefore a "theoretical maximum intake % of hydrogen" ( $H_{2,th}$ , see Table 3). Since in the Mg–Ti system also two Ti hydride phases (TiH<sub>1.924</sub> and TiH<sub>1.971</sub>) form upon hydrogenation, an additional contribution has been calculated by assuming quantitative TiH<sub>2</sub> formation.

The percentage ratio between the experimental hydrogen intake H<sub>2,tot</sub> (1st charge, i.e. after 6h isothermal/isobar at  $370 \,^{\circ}\text{C}/20 \,\text{bar}$ ) and the theoretical maximum intake  $H_{2,\text{th}}$  will be called "sorption efficiency" of the mixture. Obviously, the comparison between experimental and theoretical hydrogen intake gives a meaningful "sorption efficiency" only when the maximum equilibrium intake (under given experimental conditions) is reached, or the sorption process is completed. As it would take very long times to be sure that the H<sub>2</sub> equilibrium content has been reached, in the following we consider the absorption process to be completed if the hydrogen amount absorbed during the last hour of the 6 h isobaric stage  $(H_{2,last h})$  is less than 3% of the total hydrogen intake, i.e.  $(H_{2,\text{last h}}/H_{2,\text{tot}}) \times 100 < 3$ . With such an empirical threshold value, the hydrogen absorption of some samples (in bold in the table) cannot be considered completed in 6 h under the experimental conditions of this work.

Very high storage efficiencies are obtained for the two mixtures in the Mg–Cu system and for  $Mg_{70}Al_{30}$ . These systems show also fully reversibility at 1 bar H<sub>2</sub> pressure: this means that the sorption mechanisms described in Eq. (1) and (2) act with high efficiency and high yields in both directions.

The sorption capacities of  $Mg_{55}Al_{45}$  and  $Mg_{37}Al_{63}$  are high too, but the reversibility of the mechanism described in Eq. (3) is less than 75%.

As described above,  $Mg_{50}Zn_{50}$  has a low sorption efficiency due to kinetics limitations, while the high storage efficiency and good reversibility characterizing  $Mg_{70}Zn_{30}$  are due to the presence of "free Mg" and not to the action of Zn as a catalyst.

For all the other systems the sorption efficiencies are lower than 80% and the processes are not fully reversible.

# 4. Conclusions

In this paper, binary mixtures of Mg and nine different metals M have been prepared by ball-milling and characterized by thermogravimetric analysis (at different hydrogen pressure) and X-ray powder diffraction. The main goal of the work was to evaluate if M could act as catalyst for MgH<sub>2</sub> formation and/or as destabilizing agent towards MgH<sub>2</sub> dissociation. Mixtures with metal composition ranging from 30 up to 63 wt% have been analyzed and the intermetallic Mg–M phases formed by milling and by hydriding/dehydriding identified.

In the mixtures containing Cu, Al and Zn, the hydrogen sorption processes take place through reactions involving binary intermetallic Mg compounds. When Al and Zn are present, the sorption mechanism is different for different M contents. The storage efficiencies of these three systems are high, but only Cu seems to be effective as destabilizing agent, leading to a substantial decrease of the desorption temperature (down to 270 °C for the Cu-richer mixture). Moreover, the dissociation of MgH<sub>2</sub> takes place with appreciably higher rate than in pure Mg/MgH<sub>2</sub> system when the Cu containing phase MgCu<sub>2</sub> is present. The solid state reactions involving Al and Zn need temperatures higher than 320 °C, and take place with decreasing rates as the M content increase. All the other metals do not form intermetallics and are not directly involved in the sorption reactions; their presence reduces the storage efficiency of Mg and the reversibility of the sorption processes.

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