Structural Stability and Dehydrogenation of (MgH₂+Al, Nb) Powder Mixtures during Mechanical Alloying

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High-energy ball milling of MgH₂ with appropriate alloying elements is reported to improve the hydrogenation kinetics of MgH₂ but the relevant information on dehydrogenation is scarce. Here, a systematic study was carried out to clarify the effects of two key alloying elements, Nb and Al, on the microstructure and the dehydrogenation behaviour of the MgH₂. Intensive mechanical alloying was carried out to synthesise (MgH₂ + M) powder mixtures (M=Nb, Al). XRD Rietveld analysis revealed the formation of a new bcc phase in the (MgH₂+M) mixture and a (Al,Mg) solid solution in the (MgH₂+Al) mixture. The amount of the newly formed phase in each case increased with milling time, while the level of Nb or Al decreases. SEM analysis of the milled powders showed the existence of nano-particles within 20 hours of milling. Thermogravimetry (TG) results showed that the mechanically alloyed (MgH₂+M) mixture released about 3.9 mass% H₂ and the milled (MgH₂+Al) about 5.4 mass% H₂ at 300°C within 10 minutes, compared with only 1.5 mass% of the milled MgH₂ powder and 1.0 mass% of the as-received MgH₂ under the same conditions.

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1. Introduction

Metal hydrides are of considerable interest for safe and easy hydrogen storage. Among these, MgH₂ is considered as a very promising hydrogen storage material for vehicular applications,1) due to its high theoretical H-storage capacity of about 7.6 mass%, light weight, and low cost. However, its widespread commercial applications have been hindered by its high desorption temperature, between 300°C-400°C, a low plateau pressure of 10 Pa at ambient temperature,2,3) and slow reaction kinetics. Complete conversion of Mg to MgH₂ requires more than 50 hours at 350°C.3)

Mechanical alloying (MA) is one of the widely used methods of synthesising nanocrystalline materials. It has been used to produce nanocrystalline powders with a high specific surface area at room temperature.4,5) For the preparation of Mg-based hydrogen storage materials, MA is a promising method of enhancing the miscibility of Mg with most transition metals.6)

Recently, it has been noted that milling the hydride, instead of the metal, produces novel nano-structures with a high surface area, of great benefit to hydrogen sorption kinetics. Moreover, the presence of hydrogen in the powder is likely to reduce the level of oxidation during mechanical alloying.7) However, the dissociation of the hydrogen molecule does not occur readily on the Mg surface. The addition of a catalytic metal, such as palladium and nickel, is required to enhance the dissociation. More recently, Zaluska et al.8) have identified that the presence of other additives, such as Al, Li, Mn, Ti, V, Y and Zr, improves the hydrogen storage properties of Mg to some extent. However the improvement is still insufficient for practical applications. It is necessary to identify a most effective catalyst.

In this study, the Mg hydride was mixed with two metals, Nb and Al. There have been little efforts to investigate systematically and compare their different effects on structural characteristics and hydrogen desorption of the Mg-H system. Nb is a bcc transition element and forms two types of hydrides, NbHₓ (x < 0.9) with a bcc structure and NbH₁ with an fcc structure,9) while Al is an fcc metal and does not form a stable hydride at normal conditions. So it is important to compare the thermodynamic and kinetic modifications when milling MgH₂ with a transition metal (Nb) and a non-transition metal (Al). It is also expected that MA of MgH₂ with both Nb and Al can lead to the formation of (Mg,Nb)Hₓ and (Mg,Al)Hₓ hcp solid solutions. The dissolution of both Nb and Al into Mg should stabilise the Mg hydride and so reduce its decomposition temperature. In our previous study of a (TiH₂:22Al-23Nb) mixture,10) it was noted that a (Nb,Ti)Hₓ solid solution was readily formed within 2 hours of milling and its amount increases with milling time. It is envisaged that mechanical alloying of (MgH₂+Al) and (MgH₂+Nb) mixtures may lead to the formation of non-equilibrium solid solutions, such as hcp (Mg,Nb)Hₓ and (Mg,Al)Hₓ, or bcc (Mg,Nb,Mg)Hₓ and fcc (Al,Mg,Mg)Hₓ, respectively, with improved hydrogen storage properties.

Both (MgH₂+10 mass%Nb) and (MgH₂+10 mass%Al) mixtures, hereafter termed as (MgH₂+Nb) and (MgH₂+Al), were mechanically alloyed up to 20 hours. The micro-structures were analysed using XRD Rietveld analysis and SEM techniques. Dehydrogenation of the MA mixtures was investigated by thermogravimetry (TG). The results are discussed in terms of phase formation, crystalline structural evolution and dehydrogenation kinetics. Furthermore, a (MgH₂+50 mass%Nb) mixture was milled for 20 hours in order to study the crystalline structure of the Nb-rich hydride phase by neutron diffraction.

2. Experimental Methods

MgH₂ powder was purchased from Th. Goldschmidt AG, with a nominal composition of 95 mass%MgH₂ and...
5 mass% Mg and an average diameter of 50 μm. Elemental Al (99.5 mass%, 60 μm) and Nb (99.85 mass%, 20 μm) powders were purchased from Goodfellow. A Fritsh P5 planetary ball mill with sealed pots was used for mechanical alloying under an inert atmosphere. The elements were weighted in a glove box filled with high purity argon. Each experiment involved about 6 g of powder and 6 stainless-steel balls of 20 mm in diameter, leading to a ball-to-powder weight ratio of 30. A relatively common milling speed of 250 min⁻¹ was chosen in the study.

X-ray diffraction characterisation was performed using a D5000 Siemens diffractometer equipped with Cu Kα radiation. Qualitative and quantitative Rietveld analyses were carried out using the Rietan programme¹¹,¹² to determine the abundance, composition and lattice parameters of the phases involved.

Analyses of microstructure and chemical composition were carried out using a JEOL 6300 Scanning Electron Microscope equipped with an Oxford Instruments Energy Dispersive X-ray Spectrometer (EDX).

Thermogravimetric Analysis (TGA) was carried out using a Setaram Setsys 16/18 system, with a precision of 0.1 μg to determine the amount of hydrogen released during heating under continuous vacuum.

3. Results

3.1 X-ray diffraction analysis of crystal structure

3.1.1 XRD patterns

Figure 1 compares the X-ray diffraction patterns of the (MgH₂+Nb) mixture milled for different times. After only 2 hours of milling, new diffraction peaks, marked by ‘’H’’, were observed, which can be indexed to a bcc structure, termed as Bcc', to distinguish it from the bcc Nb. With increasing milling time, the peak intensities of the Bcc' increased while those of the bcc Nb decreased. No crystalline

![Fig. 2 Evolution of XRD patterns of the (MgH₂+10Al) mixture with milling time.](image)

Nb was detected from the XRD pattern after 20 hours of milling. The formation of a γ-MgH₂ phase (which usually exists at high pressure) was also noted after 2 hours of milling. Meanwhile, the diffraction peaks show some level of broadening due to particle size reduction and strain accumulation during milling.

For the (MgH₂+Al) mixture, Fig. 2, milling up to 2 hours led to little change of the phase structure. All the elemental constituents were still identifiable, apart from the appearance of weak γ-MgH₂ peaks. With further increase in milling time, the diffraction peaks of the original constituents were broadened and their intensities decreased, due to particle size reduction and strain accumulation. Moreover, the XRD patterns show clearly that Al diffraction peaks shift to lower angles with increasing milling time, which indicates a lattice expansion. Further analyses of the crystal structure using the Rietveld method were undertaken to clarify this point.

3.1.2 Rietveld analysis

Qualitative and quantitative phase analyses using the Rietveld method were performed based on the XRD data. During the refinements, the following assumptions were made: i) the zero shift and the instrumental parameters have been determined using the diffraction pattern of the highest accuracy standard material (Si640b) and then fixed, and ii) the metallic site occupancy was fixed for all phases according to the stoichiometry.

The criteria of fit can be evaluated by various parameters. The Goodness-of-fit indicator $S$ is defined by $S = R_wp/R_e$, where $R_wp$ and $R_e$ are the $R$-weighted patterns and the $R$-expected, respectively.¹³ Qualitative phase analysis with the Rietveld method of a multiphase sample relies on the following relationship:¹⁴

$$W_p = \frac{S_p(ZMV)_p}{\sum_{i=1}^{n} S_i(ZMV)_i},$$

where $W$ is the relative weight fraction of phase $p$ in a mixture of $n$ phases; $S$, $Z$, $M$ and $V$ are, the Rietveld scale factor, the number of formula unit per unit cell, the mass of

![Fig. 1 Evolution of XRD patterns of the (MgH₂+10Nb) mixture with milling time.](image)
the formula unit (in atomic units), and the unit cell volume (in nm$^3$), respectively.

Rietveld analysis of the as-received MgH$_2$ (Table 1) showed that it actually contained 2.04 mass% Mg, instead of the 5 mass% nominal value. Rietveld analysis of the (MgH$_2$+Nb) mixture confirmed that both the lattice parameters of the $\beta$-MgH$_2$ and the phase composition of the initial mixture varied with milling time, as shown in Table 1. The unit cell volume of the $\beta$-MgH$_2$ reduced from 0.06167 nm$^3$ in the original powder to 0.06459 nm$^3$ after 20 hours of milling. The unit cell volume of the newly formed Bcc' only changed slightly during milling. The 20h-milled mixture consisted of 80.7% $\beta$-MgH$_2$, 7.9% $\gamma$-MgH$_2$ and 11.4% Bcc'.

For the (MgH$_2$+Al) mixture, the results of the Rietveld analysis are reported in Table 2. There is little change in the lattice parameters of the MgH$_2$ phase, though the phase ratios were well modified. The relative amount of the "free" Al was found to increase while MgH$_2$ decreases with the formation of the high-temperature $\gamma$-MgH$_2$ phase. The phase composition of the mixture after 20 hours of milling is 73.1% $\beta$-MgH$_2$, 5.7% $\gamma$-MgH$_2$ and 21.2% Al. Moreover, the Al diffraction peaks shifted to lower angles with a longer milling time, indicative of a lattice expansion. The volumes of the Al unit cell are 0.06627 nm$^3$ in the starting powder, and 0.06654 nm$^3$, 0.06666 nm$^3$ and 0.06813 nm$^3$ after 2h, 10h and 20h milling, respectively. Two possibilities may account for the lattice expansion of Al: 1) dissolution of Mg into the Al lattice to form an (Al, Mg) fcc solid solution with a larger lattice parameter, which is in agreement with the difference in the atomic radii ($r_{\text{Mg}} = 0.16 \text{ nm} > r_{\text{Al}} = 0.143 \text{ nm}$); or

<table>
<thead>
<tr>
<th>Materials</th>
<th>&quot;S&quot;*</th>
<th>Lattice parameter (nm)</th>
<th>Phase composition mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received MgH$_2$ powder</td>
<td>4.39</td>
<td>$\beta$-MgH$_2$: 0.4518(0)**</td>
<td>$\beta$-MgH$_2$: 91.96</td>
</tr>
<tr>
<td>Mg:</td>
<td></td>
<td>-</td>
<td>0.3022(0)</td>
</tr>
<tr>
<td>As-received Nb powder</td>
<td>1.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg:</td>
<td></td>
<td>-</td>
<td>0.3020(0)</td>
</tr>
<tr>
<td>Mg:</td>
<td></td>
<td>-</td>
<td>0.3027(1)</td>
</tr>
<tr>
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</tr>
</tbody>
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**: Values indicated in brackets represent the estimated standard deviation.

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Table 1 XRD Rietveld analysis of the (MgH$_2$ + 10Al) mixture.

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<td>-</td>
<td>0.3022(0)</td>
</tr>
</tbody>
</table>

*: Goodness-of-fit.

**: Values indicated in brackets represent the estimated standard deviation.
ii) the dissolution of MgH$_2$ into Al to form an (Al,Mg)H$_x$ solid solution with an fcc structure as similarly observed in a (TiH$_2$-22Al-23Nb) system where a (Nb,Ti)H$_x$ bcc solid solution was formed. Both mechanisms support the apparent increase in the amount of the “free” Al with milling time.

### 3.2 Effects of MA on microstructure

Qualitative investigation of particle morphology and size of the milled powder was carried out using SEM. Figure 3 shows that particle size was significantly reduced after milling of both the (MgH$_2$+Al) and the (MgH$_2$+Nb) mixtures, compared with the starting elemental powders. The relatively hard and brittle hydride largely assisted the breaking of all the particles in the mixtures. The particle morphology is typical of agglomerated nano-particles, instead of deformed and welded particles observed frequently in ductile metal powder.

### 3.3 Thermogravimetric analysis

Figure 4 compares the hydrogen desorption characteristics of various milled samples during an isothermal holding at $T = 300^\circ$C under a vacuum of 0.25 Pa. The curve for the as-received MgH$_2$ was also shown for comparison. It is noted that both the mechanically alloyed (MgH$_2$+Al) and (MgH$_2$+Nb) mixtures reach an equilibrium state within 4.8 to 6.2 $\times$ 10$^2$ s of dehydrogenation. The amount of H$_2$ released after 10 minutes is about 1.0, 1.5, 3.9 and 5.4 mass% for the as-received MgH$_2$, the milled MgH$_2$, the milled (MgH$_2$+Nb) and the milled (MgH$_2$+Al), respectively.

The sudden abnormal weight gain at the beginning of the desorption curves of the latter two cases is likely due to the effect of a certain degree of oxidation of the metallic additions, whereas the other two samples, essentially consisting of the relatively stable hydride, show little tendency of oxidation at the low temperature. The TG vacuum was in fact very high, 0.25 Pa, with a very low oxygen partial pressure or residue, and it is unlikely that the oxidation will continue to play a role in the mass change, once the initial oxygen is consumed to form a thin/stable layer on the metal additions at the top of the powder samples.

### 4. Discussion

#### 4.1 (MgH$_2$+Nb) mixture

The evolution of the $\beta$-MgH$_2$, the Bcc’ and the Nb is shown in Fig. 5 with milling time. It is clearly seen that the
amount of the newly formed phase Bcc' increases while those of the $\beta$-MgH$_2$ and the Nb decrease with increasing milling time. The following possible reactions may be involved:

\begin{align}
\text{Reaction I:} & \quad \text{Mg + Nb} \rightarrow (\text{Nb,Mg}) \\
\text{Reaction II:} & \quad \text{MgH}_2 + \text{Nb} \rightarrow \text{MgH}_2\text{--} + \text{Nb}_x \\
\text{Reaction III:} & \quad \text{MgH}_2 + \text{Nb} \rightarrow \text{MgH}_2\text{--} + (\text{Nb,Mg})_x
\end{align}

The Reaction I involves residual pure Mg in the MgH$_2$ powder, as shown in the X-ray diffraction pattern (Fig. 1) and confirmed by the Rietveld analysis (Table 1). Although the equilibrium Mg-Nb phase diagram shows that the solubility of Mg in solid Nb was about 0.04 mass\%, the (Nb,Mg) bcc solid solution can absorb more hydrogen under non-equilibrium high energy milling conditions. The lattice parameter of the solid solution should increase with increasing content of Mg in Nb. The XRD patterns of the (MgH$_2$+Nb) mixture show that the positions of new diffraction peaks do not seem to change with milling time after 2 hours of milling. The Rietveld analysis confirms that the lattice parameter of the newly formed phase only changes slightly, while its amount increases with milling time. The relative lattice expansion is about 4.1% from bcc-Nb to Bcc'. It is noted that the atomic radius of Mg is larger than that of Nb, $r_{\text{Mg}} = 0.16$ nm > $r_{\text{Nb}} = 0.145$ nm, and a lattice expansion is expected when Mg is in solution of Nb. Hence, the Bcc' phase could be attributed to a (Nb,Mg) solid solution. There may be a maximum solid solubility of Mg into Nb, which was reached within 2 hours of milling under the specific conditions, and hence no further change of lattice parameters upon prolonged milling.

Both of the possible Reactions II and III are likely to be responsible for the formation of the Nb-based hydride phase and neither can be ruled out completely. The second reaction suggests that H$_2$ will migrate from MgH$_2$ to Nb via a diffusion mechanism to form progressively the Nb$_x$H$_y$, where the process involves atomic hydrogen diffusion into Nb from the bulk of MgH$_2$ across the MgH$_2$/Nb interface. Although (equilibrium) thermodynamics may disfavour the formation of NbH$_y$ by this route, as MgH$_2$ is slightly more stable than NbH$_x$ (formation energy of: MgH$_2 = 75$ kJ/mol, and NbH$_x = 60$ kJ/mol), mechanical energy (gradient) during mechanical alloying can provide sufficient activation and effectively enhances hydrogen migration towards Nb. Also both hydrides are non-stoichiometric compounds and their activities (or stabilities) depend very much on the hydrogen content. A previous observation by Pellitter et al. has also suggested the formation of a NbH$_x$ ($x = 0.6$) when MgH$_2$ is milled with 5 at% Nb. Reaction III involves solid state reaction between Nb and MgH$_2$ to form a (Nb,Mg)H$_y$ solid solution, which can be promoted again by mechanical energy gradient during the high energy milling process.

If the newly formed phase with a bcc type structure is an intermediate Nb hydride, the following expression showing the evolution of the NbH$_x$ lattice parameter with hydrogen content reported earlier$^{17}$ can be used to estimate the hydrogen content in the hydride:

$$\left(\frac{\Delta a}{a}\right) = (4.72 \pm 0.25) \times 10^{-4} \text{ per at\% (H/Nb)},$$

where $a$ is the lattice parameter of the hydrogen-free Nb (as-received Nb powder), $\Delta a$ is the change in the lattice parameter due to hydrogen atoms. The lattice expansion corresponds to the stoichiometric hydride NbH$_{5.83}$.

Moreover, it is also important to note that during MA of the (MgH$_2$+Nb) mixture, a certain amount of low-temperature tetragonal $\beta$ phase transforms into the high-pressure orthorhombic $\gamma$ phase:

$$\beta\text{-MgH}_2 \rightarrow \gamma\text{-MgH}_2.$$  

From the literature, it is noted that the $\beta$-phase transforms into a $\gamma$-phase after being treated at high pressures (2.5 to 8 GPa) and high temperatures (250 to 900°C) for 1 to 3 hours. It is also reported that the $\beta$-MgH$_2$ phase partially transforms into a metastable $\gamma$-MgH$_2$ phase under a high compressive stress. The transformation starts at $P = 2.5$ GPa where the two phases coexist up to 8 GPa. The $\beta$-phase transforms totally to the $\gamma$-phase on heating up to 350°C.

More recently, an investigation performed under a high pressure shows that $\beta \rightarrow \gamma$ transformation occurs at a pressure of 8 GPa and a complete transformation to the $\gamma$ phase is achieved at pressures greater than 10 GPa.$^{19}$

Huot et al.$^{20}$ have reported that after ball milling of MgH$_2$ using a Spex 8000 shaker mill with a ball-to-powder ratio of 10:1, the $\gamma$-MgH$_2$ phase is formed and its amount reaches a maximum of 18 mass\% after 2 hours of milling. MA is a well-known processing route for the synthesis of metastable phases. The polymorphic transformation, $\beta \rightarrow \gamma$, within the MgH$_2$ is thus a result of such an effect. Here about 8 mass\% $\gamma$ phase was obtained in the (MgH$_2$+Nb) mixture after 20 hours of milling. Huot et al.$^{20}$ also note that the disappearance of the $\gamma$ phase after cycling does not change the kinetics, indicating that the $\beta \rightarrow \gamma$ phase transformation has little influence on the dehydridding kinetics of MgH$_2$. However, Gennari et al.$^{21}$ suggest that the presence of the $\gamma$-MgH$_2$ produces a synergetic effect during hydrogen desorption, which stimulates $\beta$-MgH$_2$ decomposition at low temperatures.

Furthermore, a Nb-rich composition (MgH$_2$+50 mass\%Nb) was prepared. The XRD pattern of the mixture milled for 20 hours (Fig. 6) showed the formation of a “composite” material containing mainly MgH$_2$ and the intermediate Bcc'. In Table 3, Rietveld analysis indicates that
the amount of the Bcc phase is 66.5 mass%, higher than that of the \(\text{C}12\)-\(\text{MgH}_2\), 33.51 mass%.

4.2 \((\text{MgH}_2 + 10\ \text{Al})\) mixture

For the \((\text{MgH}_2 + \text{Al})\) mixture, the evolution of the \(\text{C}12\)-\(\text{MgH}_2\) and Al phases with milling time is reported in Fig. 7. It is clearly shown that with increasing milling time, the amount of Al increases while both \(\beta\)-\(\text{MgH}_2\) and Mg decrease. Regarding the phase composition as well as the change in the Al lattice parameter, the following reactions may be proposed, similar to the previous case:

- **Reaction I:** \(\text{Mg} + \text{Al} \rightarrow (\text{Al},\text{Mg})\),
- **Reaction II:** \(\text{MgH}_2 + \text{Al} \rightarrow \text{MgH}_2 - x + \text{AlH}_x\),
- **Reaction III:** \(\text{MgH}_2 + \text{Al} \rightarrow \text{MgH}_2 - x + (\text{Al},\text{Mg})\text{H}_x\).

From the Mg-Al phase diagram,\(^{15}\) the maximum solubility of Mg in Al is 18.9 at\% at the eutectic temperature of 450 °C and about 1.0 at\% at room temperature. Since pure Mg exists in the as-received \(\text{MgH}_2\) powder, and both the lattice parameters and the amount of Al increase with milling time, the formation of (Al, Mg) solid solution is possible. The evolution of the Al lattice volume with milling time is shown in Fig. 8, which clearly shows a volume expansion. This may be due to the increased level of Mg in Al, as the Mg atom is larger than Al.

There is no stable Al hydride at normal conditions. Hence the second reaction may be excluded from further consideration. The reaction of \(\text{MgH}_2\) with Al during milling to form an intermediate (Al, Mg) hydride may be envisaged. However, there is no firm evidence for this mechanism. Neutron diffraction is the only technique allowing the determination of the Mg content in solution of Al and location of interstitial hydrogen atoms in the compound.

From the XRD diffraction patterns, Fig. 2, it is noted that the Al peaks are broadened with increasing milling time. Then, from the Rietveld analysis, mechanical strain accumulated during MA can be determined\(^{22}\) using the following equation:

\[
\varepsilon = \frac{\pi}{18000} \cdot (y - y_i) \cdot 100\%.
\]  \(\text{(10)}\)

where \(\varepsilon\) is the microstrain (%), \(y\) and \(y_i\) are the Lorentzian isotropic-broadening coefficients for the sample and the instrument (X-ray diffractometer), respectively. Both \(y\) and \(y_i\) are determined from the best Rietveld fit. Figure 9 shows the evolution of microstrain for both Al and \(\text{MgH}_2\) with milling time. It is clearly seen that the accumulated strains increase with milling time. The strain is much greater in Al than in \(\text{MgH}_2\), e.g. 48% higher after 2 hours of milling. The large difference may be attributed to the lattice distortion as a result of the dissolution of Mg, with an atomic radius about 12%
larger than that of Al, in Al to form an fcc - (Al, Mg) solid solution.

5. Conclusions

MgH$_2$ was mechanically milled with 10 mass% of Nb and Al, respectively. XRD patterns of the milled mixtures reveal the formation of a new bcc phase in the (MgH$_2$ + 10Nb) mixture. With the Nb addition, the new bcc phase may either be a (Nb, Mg), or a NbH$_x$, or a (Nb,Mg)H$_x$ hydride solid solution. Whereas in the case of Al, the formation of an (Al, Mg) fcc solid solution is most likely to occur. Rietveld analysis indicates that the amount of the bcc phase or the (Al, Mg) solid solution increases with milling time, while Nb or Al decreases. Microstructural observation shows very fine particles and homogeneous size distribution after milling. Mechanically milled powder mixtures exhibit improved kinetics and desorption capacity, compared to the single phase MgH$_2$ milled under identical conditions. Dehydrogenation at 300°C of the samples milled for 20 hours show that the (MgH$_2$+10Al) mixture releases 5.4 mass% hydrogen and the (MgH$_2$+10Nb) mixture 3.9 mass%, whereas only 1.5 mass% hydrogen was released from the milled MgH$_2$ powder and 1 mass% from the as-received MgH$_2$ powder. This clearly demonstrates the beneficial effects of the two alloying elements as well as mechanical alloying on hydrogen desorption (note that the total theoretical capacity of the hydride was not reached under the dehydrogenation temperature, 300°C, for a short time).

Acknowledgements

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