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Mg_2FeH_6-based Nanocomposites with High Capacity of Hydrogen Storage Processed by Reactive Milling

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The compound Mg_2FeH_6 was synthesized from a 2Mg-Fe mixture in a single process through high-energy ball milling under hydrogen atmosphere at room temperature. The complex hydride was prepared from Mg powder and granulated or powdered Fe using a planetary mill. The phase evolution during different milling times was performed by X-rays diffraction technique. The dehydrogenation behavior of the hydride was investigated through simultaneous thermal analyses of differential scanning calorimetry and thermogravimetry coupled with mass spectrometer. The use of powdered iron as starting material promoted conversion to complex hydride at shorter milling times than when granulated iron was used, nevertheless, after 24 hours of milling the 2Mg-Fe (powdered or granulated) mixtures presented similar dehydrogenation behavior. The hydrogen absorption during milling was on average 3.2 wt. (%), however, changing the proportions of the reagents to 3Mg-Fe a Mg_2FeH_6-MgH_2 based nanocomposite with higher density of hydrogen (5.2 wt. (%)) was obtained.

Keywords: *hydrogen storage materials, magnesium complex hydrides, mechanochemical synthesis*

1. Introduction

Magnesium is an attractive material to hydrogen storage due to several advantages, such as its abundance on the Earth's crust, its low cost and the high hydrogen storage capacity of its hydride (7.6 wt. (%)). However, its main drawbacks are its high stability and slow hydrogen sorption kinetics. In this context, the magnesium complex hydrides appear as an interesting alternative, compromising hydrogen storage capacity for better absorption – desorption kinetics. In this compounds group, the Mg_2FeH_6 stands out because it presents the highest known volumetric density of 150 kg of $H_2.m^{-3}$, which is more than two times higher than liquid hydrogen (70.8 kg of $H_2.m^{-3}$) one[1]. However, as Mg and Fe do not form any intermetallic compound[2], the synthesis of this complex hydride is not trivial.

In the first report concerning the synthesis of this hydride, sintering processes of Mg and Fe powders under H_2 pressure were used to obtain Mg_2FeH_6[3]. Although using high hydrogen pressures, elevated temperatures and several days, the yield of the complex hydride was only 50 wt. (%) and the sintered sample had to be purified by a complicated procedure. A processing route to reduce these severe conditions is the mechanical alloying of precursory materials before sintering[4], furthermore, a direct synthesis of the hydride can be obtained when the milling is performed under a hydrogen pressure (Reactive Milling-RM)[5,6]. This mechanically activated method can reduce the grain and particles sizes to nanometric scale and improve the hydrogen sorption kinetics of the hydrides[7,8].

The synthesis of the ternary complex hydride, Mg_2FeH_6, using ball milling from the stoichiometric compositions 2Mg-Fe or $2MgH_2$-Fe were also studied using different milling conditions[9-16]. Regardless of the milling condition, a remaining iron was always present after milling, which represents an incomplete reaction of hydride formation and results in a lower hydrogen density.

In an attempt to improve the yield of Mg_2FeH_6 formation and the hydrogen storage capacity, several papers reported the synthesis of Mg_2FeH_6 applying ball milling procedures using different proportions of the precursors Mg-Fe or MgH_2-Fe[17-20]. Nonetheless, these papers presented some controversial results. As an example, Herrich et al.[18] claimed a 92 wt. (%) yield of Mg_2FeH_6 after reactive milling of $3.5MgH_2$:Fe, even if the maximum theoretical yield of Mg_2FeH_6 phase at this reactant ratio is 74 wt. (%).

In the present paper we systematically evaluated the synthesis and the influence of the type of reagent Fe on the formation of Mg_2FeH_6 through reactive milling of 2Mg-Fe mixtures. The decomposition behavior and the amount of hydrogen of the hydrides were also studied. In order to obtain a complete reaction of the metallic elements and consequently a higher hydrogen gravimetric density, we also performed the reactive milling of a 3Mg-Fe mixtures under hydrogen pressure.

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2. Experimental

The complex hydride Mg_2FeH_6 was synthesized from a 2Mg-Fe mixture by high-energy ball milling under hydrogen pressure. Magnesium powder (–20 + 100 mesh, 99.8%), iron powder (–22 mesh, 99.998%) and iron granules (1-2 mm, 99.98%), were provided by Alfa Aesar. Magnesium was mixed with granulated or powdered iron and loaded into a stainless steel vial of 160 cm^3. After three atmosphere cleaning cycles, consisting of evacuation and argon injection, the milling vial was filled with hydrogen (99.999%) at 3MPa of pressure. In all experiments, the ball-to-powder weight ratio was 40:1. The reactive millings were carried out in a Fritsch Pulverissette P6 planetary mill at rotation speed of 600 rpm during different milling times (1 up to 72 hours). The vial was not recharged with hydrogen during the milling experiments and all samples were manipulated inside an argon filled glove box.

X-rays diffraction (XRD) measurements were performed on a Rigaku Geigerflex difractometer equipped with a graphite monochromator with Cu Kα radiation. The XRD patterns were also used to estimate the mean crystallite size through Scherrer analysis[9]. Scanning electron microscopy (SEM) images were obtained in Phillips XL 30 FEG microscope.

The dehydrogenation behavior of the hydride was investigated in a Netzsch STA 449 Jupiter® through simultaneous thermal analysis of differential scanning calorimetry (DSC) and thermogravimetry (TG) coupled with quadrupole mass spectrometer (QMS). The heating rate was 10 °C/min, using about 10 mg of sample in each experiment.

3. Results and Discussion

3.1. *Synthesis of Mg_2FeH_6*

Figure 1 presents the phases evolution in the XRD patterns of the 2Mg-Fe (Fe powder or granulated) mixtures milled under hydrogen pressure as function of milling time.

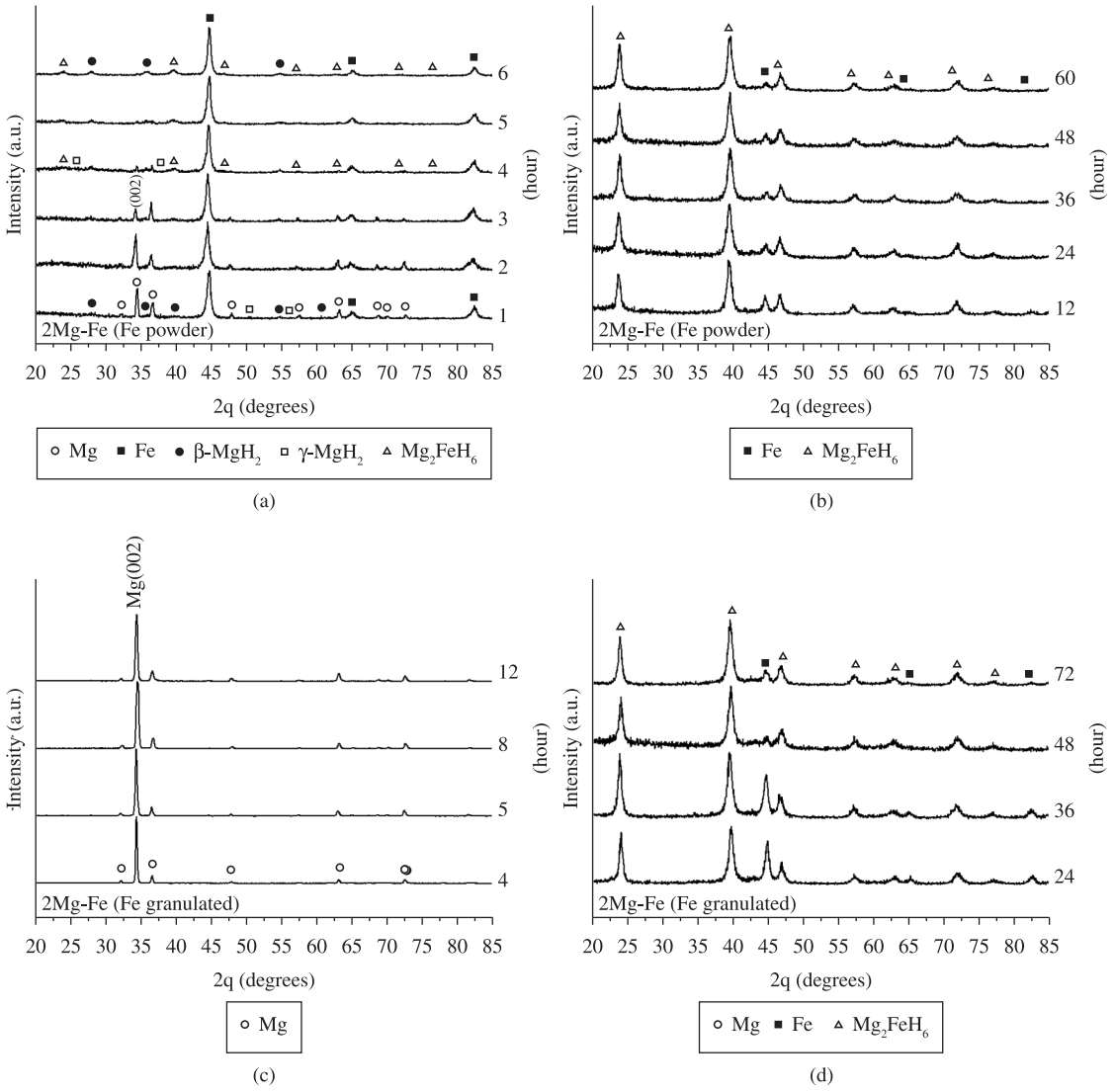


Figure 1. XRD patterns of the 2Mg-Fe mixtures milled during different milling times. a,b) Fe powder; c,d) Fe granulated.

The analysis of Figure 1a, when powdered iron is used as starting material, shows that the tetragonal β-MgH_2 (JCPDS 74-0934) is already present in the mixture after 1 hour of milling. The formation of the Mg_2FeH_6 phase (JCPDS 38-0843) starts after 4 hours of milling and the metastable orthorhombic γ-MgH_2 (JCPDS 35-1184) was also detected in the XRD pattern. The γ-MgH_2 phase formation synthesized at room temperature by ball milling was also reported in others papers[19,21]. Its formation is related to the high energy impact of the balls in the high energy ball milling process. In the mixture milled for 6 hours almost all Mg (JCPDS 35-0821) is consumed for the formation of β-MgH_2. After 12 hours of milling (Figure 1b), the powder is constituted mainly by Mg_2FeH_6 and α-Fe phases, and the increase of the milling time to 24 hours promoted a slight decrease of the iron peak intensity related to the complex hydride one. No change in the phase evolution was observed through XRD increasing the milling time.

In the case of the 2Mg-Fe (Fe granulated), the mixtures reactively milled during 4 up to 12 hours were obtained as flakes (Figure 2), and the XRD patterns, as shown in Figure 1c, show diffraction peaks preponderantly due to the planes of Mg phase. This is related to the use of granulated iron as precursory material and the tendency of the particles weld together in the shorter milling times[22]. After 24 hours of milling (Figure 1d), the product was obtained as powder formed mainly by Mg_2FeH_6 and α-Fe phases. Despite 72 hours of milling, a remaining iron was identified in the sample by XRD.

Regardless of the precursory iron type, the 2Mg-Fe mixtures processed through reactive milling presented a non-reacted iron even after long times of processing. This residual iron is an indicative of an incomplete reaction of hydride formation and results in a lower hydrogen gravimetric density due to its high atomic weight.

Table 1 presents the estimated mean crystallite sizes for the complex hydride Mg_2FeH_6 from the broadening of its respective XRD peaks.

After 24 hours of reactive milling, regardless of the type of reagent Fe (powder or granules), the mean crystallite sizes of the complex hydride range from 12 to 14 nm. These results show that is possible to achieve a comparable material in terms of mean crystallite size using a much cheaper precursory material (Fe granulated) through reactive milling.

The 2Mg-Fe (Fe powder) sample prepared by reactive milling during 60 hours was selected for SEM analysis. The micrographs of SEM are presented in Figure 3.

The SEM images shows that the powder has a sponge-like structure and it is formed by agglomerates of much smaller particles, with diameters which can reach even 20 nm, as seen in Figure 3. It is possible also to note in

Table 1. Estimated mean crystallite size of Mg_2FeH_6 as function of milling time of 2Mg-Fe mixtures.

Milling time (hour)	Mg_2FeH_6 Crystallite Size (nm)	
	2Mg-Fe (Fe powder)	2Mg-Fe (Fe granulated)
6	17	-
12	13	-
24	12	13
36	12	13
48	13	14
60	12	-
72	-	12

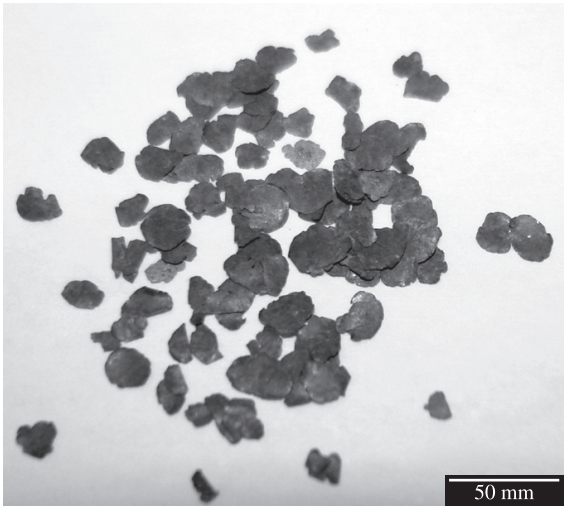
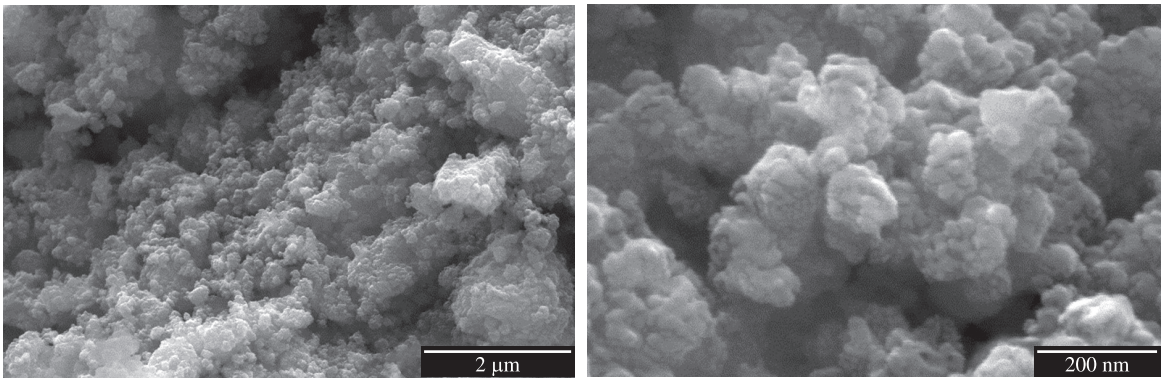


Figure 2. Flakes obtained by the reactive milling of 2Mg-Fe (Fe granulated) mixture during 12 hours.



(a) (b)

Figure 3. SEM images using secondary electrons of 2Mg-Fe (Fe powder) sample milled under hydrogen pressure for 60 hours. a) sponge-like structure, b) particles full of asperities.

Figure 3b that the surface of the bigger particles is full of asperities. This surface morphology presented by the powders is interesting for hydrogen storage applications, since high surface specific area values benefits fast hydrogen sorption kinetics.

3.2. *Dissociation of Mg_2FeH_6*

The dehydrogenation behavior of the 2Mg-Fe mixtures reactively milled during different milling times was studied by simultaneous thermal analyses of DSC and TG, and the curves are presented in Figures 4 and 5, respectively. Results of XRD and simultaneous thermal analyses of MgH_2 prepared from magnesium powder through reactive milling using the same processing parameters are shown in Figure 6 for comparison.

The DSC curve of the 2Mg-Fe (Fe powder) sample milled for 6 hours presented only one endothermic peak related to the hydrogen release, as shown in Figure 4a, nonetheless, α-Fe and two hydride phases, Mg_2FeH_6 and MgH_2, were identified through XRD (Figure 1a). This decomposition thermal behavior indicates a reaction peak overlap. Analyzing the higher desorption temperature range for the MgH_2 in Figure 5b, we can suggest that the presence of α-Fe and Mg_2FeH_6 in the powder destabilized the MgH_2 structure, lowering its hydrogen desorption temperature. As reported by Zhou et al.[14], the Mg_2FeH_6 can reduce the structural stability of MgH_2 and further improve its dehydrogenation properties.

Longer milling times than 6 hours promote higher conversion of the Mg_2FeH_6 from MgH_2 and α-Fe, and consequently the DSC peak is dislocated to higher temperatures up to 24 hours of milling. Additional milling times reduce the decomposition peak temperature up to 48 hours, nonetheless, the 2Mg-Fe (Fe powder) milled for 60 hours presented a higher hydrogen desorption temperature, which could be attributed to some contamination from the vial and the balls as a result of the long milling time.

The same hydrogen desorption behavior is observed for the 2Mg-Fe (Fe granulated) samples in Figure 4b, however, it does not occurs in the same milling times than the 2Mg-Fe (Fe powder) samples due to the differences in the milling times to the conversion of the Mg_2FeH_6.

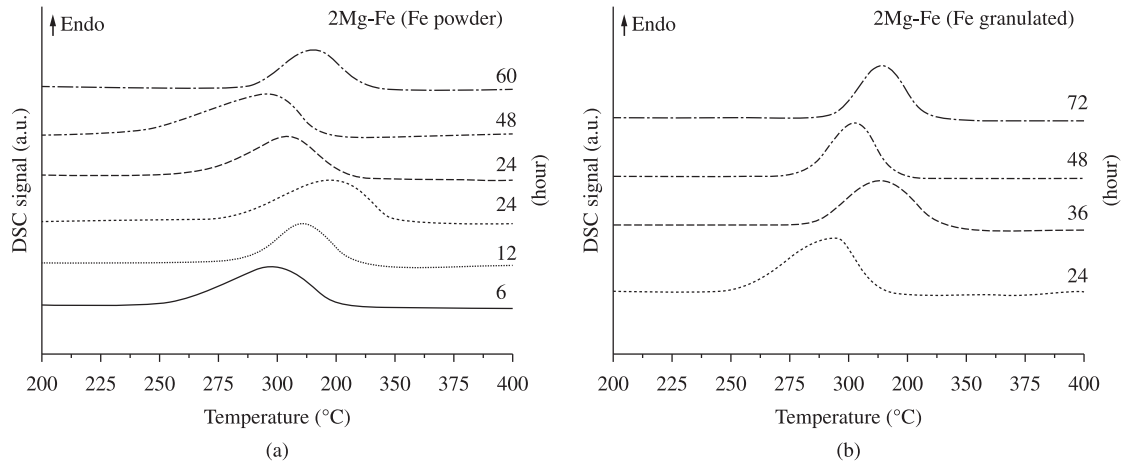


Figure 4. DSC curves of 2Mg-Fe mixtures milled during different milling times. a) Fe powder, and b) Fe granulated.

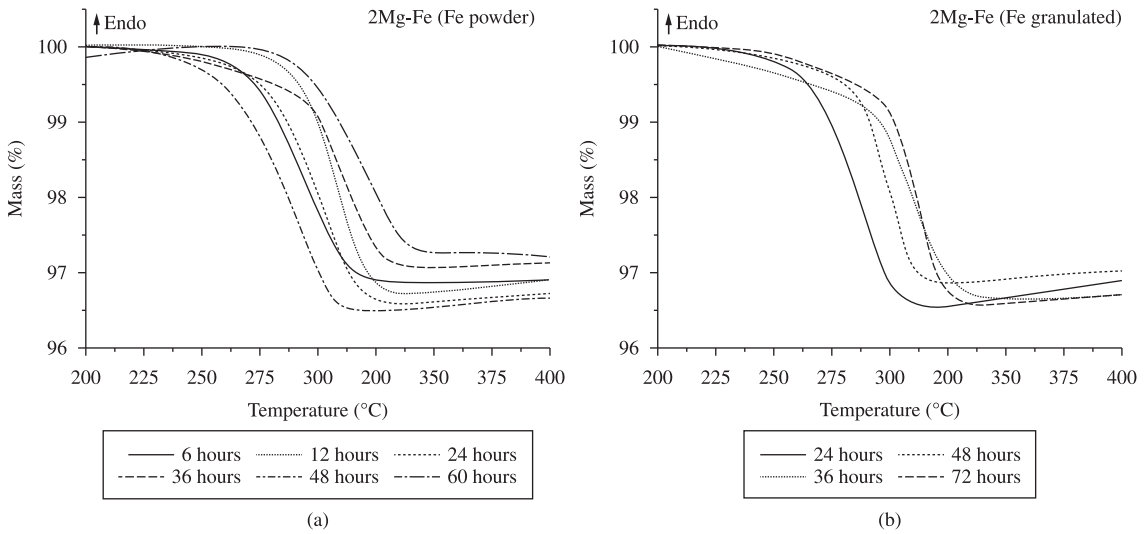


Figure 5. TG curves of 2Mg-Fe mixtures milled during different milling times. a) Fe powder, and b) Fe granulated.

The hydrogen gravimetric capacities measured through TG analyses of the 2Mg-Fe samples were on average 3.2 wt. (%), as depicted in Figure 5. This result represents only 60% of the theoretical hydrogen capacity of Mg_2FeH_6 (5.4 wt. (%)) and it is associated to the presence of the remaining iron in the powder.

3.3. *Reactive milling of 3Mg-Fe*

The low hydrogen gravimetric capacities measured through TG (Figure 5) are related to the presence of the remaining iron in the powders, as identified by XRD (Figure 1). These results are explained based on the reaction sequence for the formation of Mg_2FeH_6 proposed by Gennari et at.[5]:

$$Mg_{(s)} + H_{2(g)} \Leftrightarrow MgH_{2(s)} \quad (1)$$

$$3MgH_{2(s)} + Fe_{(s)} \rightarrow Mg_2FeH_{6(s)} + Mg_{(s)} \quad (2)$$

In the second reaction, the proportion of MgH_2 and Fe is 3:1.Therefore, in a 2Mg-Fe composition, the $2MgH_2$ synthesized from 2Mg will react with 2/3 of the Fe, remaining 1/3 of the Fe in the powder. Consequently, the products of the second reaction will be $2/3Mg_2FeH_6$, 1/3Fe and Mg. The theoretical hydrogen gravimetric capacity of this compound is 3.6 wt. (%), which agrees with ours TG results as presented in Figure 5. We also have to consider that MgH_2 might be formed from Mg in the reactive milling process. The identification through XRD of Mg or even MgH_2 in the powder is difficult due to their small crystallite size, low volumetric fraction and low electron density in comparison to Mg_2FeH_6 and Fe.

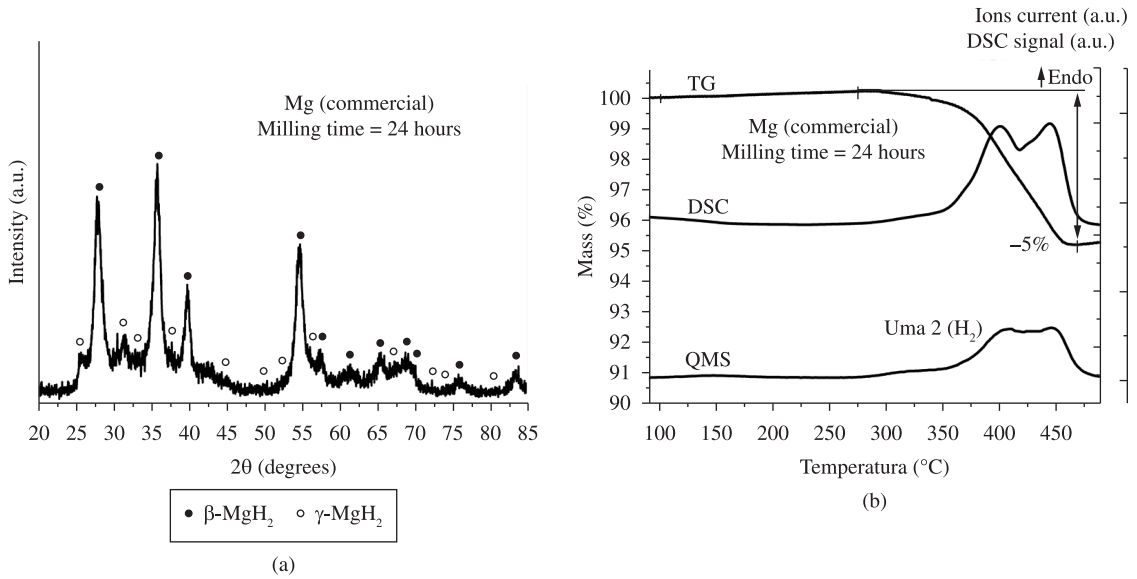


Figure 6. a) XRD pattern, and b) DSC, TG and QMS curves of MgH_2 prepared by reactive milling.

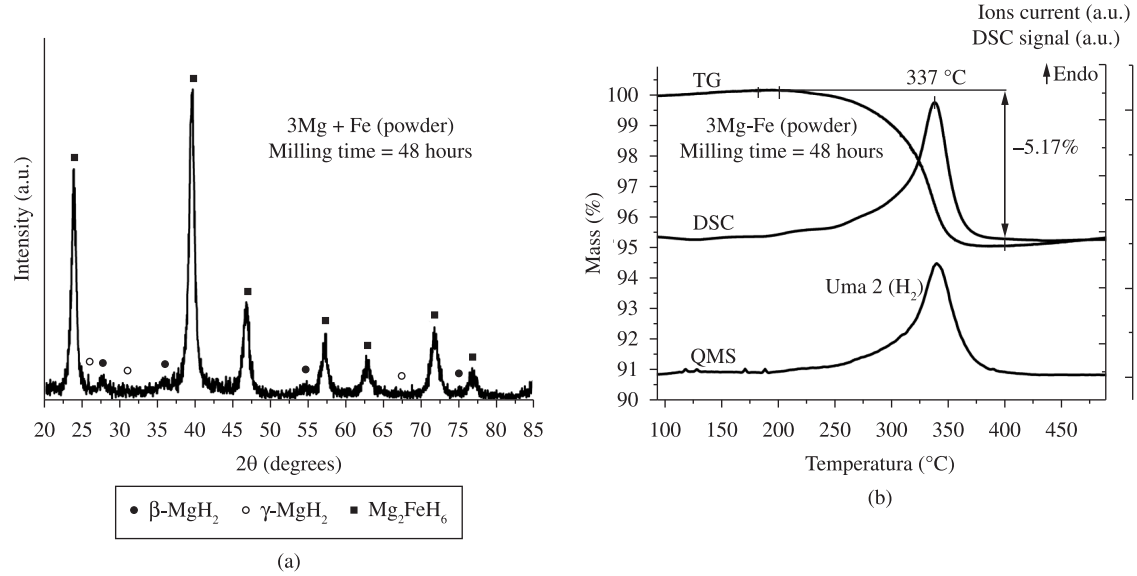


Figure 7. Results of the 3Mg-Fe (Fe powder) composition milled under hydrogen pressure. a) XRD pattern. b) DSC, TG and QMS curves.

Aiming a complete reaction of the metallic elements and a higher hydrogen gravimetric density due to the presence of MgH_2 and Mg_2FeH_6, we changed the proportion of the reagents to 3Mg:Fe. This composition was milled during 48 hours under hydrogen pressure using the same conditions applied to the 2Mg-Fe mixtures.

After the reactive ball milling, the 3Mg-Fe powder presented a greenish color while the 2Mg-Fe one had a black/dark gray color. A green color was also reported when sintering process was used to synthesize Mg_2FeH_6 from a 2Mg-Fe composition[3,4].

Figure 7a shows that the 3Mg-Fe powder is mainly constituted by the Mg_2FeH_6 phase, having a mean crystallite size of 13 nm. The β-MgH_2 phase was also identified in the XRD pattern. The most interesting result was that the α-Fe phase was kept to a minimum, indicating a high yield of the Mg_2FeH_6 synthesis. In the others papers concerning the synthesis of Mg_2FeH_6 from a 3Mg-Fe or $3MgH_2$-Fe composition through ball milling[17-19], the α-Fe phase is easily identified in the XRD pattern. Moreover, in all these papers the milling times were longer than 60 hours.

The simultaneous thermal analysis curves are presented in Figure 7b. The hydrogen desorption starts at a temperature lower than 200 °C and reaches its peak at 338 °C. Furthermore, a hydride duplex phase, Mg_2FeH_6-MgH_2, was identified through XRD (Figure 7a); nonetheless, only one endothermic peak in the DSC curve (Figure 7b) represents the hydride decomposition. This thermal behavior indicates a reaction peaks overlap and it is explained by the fact of the Mg_2FeH_6 can reduce the structural stability of MgH_2 and further improve its dehydrogenation properties[14].

The TG analysis curve shows that the hydrogen gravimetric capacity is 5.2 wt. (%). This is one the highest hydrogen gravimetric capacity reported using a single step procedure through reactive milling under hydrogen pressure of magnesium and iron as precursory materials.

Considering the theoretical hydrogen capacity of the 3Mg-Fe mixture (5.8 wt. (%)), the measured gravimetric capacity after the reactive milling represents a 90% yield of the hydride formation. The higher hydrogen gravimetric capacity of the 3Mg-Fe sample in comparison to the 2Mg-Fe one is related to the complete reaction of the metallic elements with the hydrogen and the presence of the MgH_2 phase.

4. Conclusions

In this paper we studied the formation of the complex hydride Mg_2FeH_6 by reactive milling of 2Mg-Fe mixtures under hydrogen pressure. The influence of type of the reagent Fe on the formation of Mg_2FeH_6 was also evaluated. The use of powdered iron as starting material promoted conversion to complex hydride at shorter milling times than when granulated iron was used, nonetheless, after 24 hours of milling the 2Mg-Fe (Fe powder or granules) mixtures presented similar mean crystallite size and dehydrogenation behavior. Even after 72 hours of milling, a remaining iron was identified through XRD and the hydrogen gravimetric capacity was on average 3.2%, however, changing the proportions of the reagents to 3Mg:Fe a Mg_2FeH_6-MgH_2 based nanocomposite was obtained with higher hydrogen storage capacity (5.2 wt. (%)).

Acknowledgements

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