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Effective synthesis of Mg_2CoH_5 by reactive mechanical milling and its hydrogen sorption behavior after cycling

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ARTICLE INFO

Article history:
Received 15 August 2012
Received in revised form
11 October 2012
Accepted 14 October 2012
Available online 17 November 2012

Keywords:
Hydrogen storage
Hydride
Mechanical milling
Magnesium
Complex hydride

ABSTRACT

Mg_2CoH_5 was synthesized by reactive mechanical milling (RMM) under hydrogen atmosphere (0.5 MPa) from $2MgH_2$–Co and $3MgH_2$–Co mixtures, with a yield >80%. The microstructure, structure and thermal behavior of the phases formed during the processing were investigated by transmission electron microscopy, X-ray diffraction and differential scanning calorimetry. Kinetic properties of the reaction with hydrogen of the $2MgH_2$–Co and $3MgH_2$–Co mixtures after RMM were evaluated using modified Sieverts-type equipment. The $3MgH_2$–Co mixture showed better properties for storage applications, with its highest rate of hydrogen absorption and desorption at 300 °C, its storage capacity of about 3.7 wt% in less than 100 s, and good stability after cycling. Although the starting material presents Mg_2CoH_5 as majority phase, the cycling leads to disproportion between Mg and Co. We obtained a mixture of Mg_2CoH_5, $Mg_6Co_2H_{11}$ and MgH_2 hydrides, as well as other phases such as Co and/or Mg, depending on experimental conditions.

1. Introduction

Metal hydrides are an excellent alternative for hydrogen storage, since they are able to concentrate a high amount of hydrogen per unit volume and final mass. In particular, the Mg–Co–H system is interesting because, depending on the experimental conditions, it allows the formation of MgH_2 [1,2] as well as two complex hydrides: the tetragonal β-Mg_2CoH_5 [1] and the orthorhombic γ-$Mg_6Co_2H_{11}$ [2,3]. The β-Mg_2CoH_5 hydride was discovered by Zolliker et al. [1], who first characterized its structure as a distorted tetragonal CaF_2 type which changes into a disordered cubic one at temperatures around 200 °C [1,2]. The low temperature hydride was initially referred to as Mg_3CoH_5 and characterized with an hexagonal structure [2]. Cerny et al. finally found that the structure was orthorhombic, with a stoichiometric composition of $Mg_6Co_2H_{11}$ [3]. From a technological point of view, the $Mg_6Co_2H_{11}$ and Mg_2CoH_5 hydrides are attractive for storage applications due to their high gravimetric (4.0 wt% and 4.5 wt % of hydrogen, respectively) and volumetric (>90 kg m^{-3}) hydrogen storage capacity [4–6]. Moreover, the complexity of the system with different hydride phases and the absence of stable precursors, such as Mg_2Co or Mg_3Co to produce a single hydride phase [7], are the main reasons for the scarce knowledge about the Mg–Co–H system. In addition, little is known about the absorption and desorption kinetics, as well as about hydrogen storage reversibility of $Mg_6Co_2H_{11}$ as Mg_2CoH_5.

Although various synthetic methods have been carried out to prepare hydrides of Mg and Co, the sintering method (heat

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0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2012.10.086

treatment with high hydrogen pressure for a long time) is the most used [1,2,4,6,8,9]. However, to achieve high yields of the desired complex hydride, it is usually necessary to have an homogeneous mixing degree of the starting materials (Mg and Co). For this reason, the sintering process is used in combination either with the mechanical milling under argon (MM, pre-grinding of materials) or reactive mechanical milling (RMM) under hydrogen. Ivanov et al. [1,2] synthesized both Mg_2CoH_5 and $Mg_6Co_2H_{11}$ by MM of 2Mg-Co powders followed by a treatment for several days in an autoclave at temperatures and pressures not reported. Huot et al. [9] have synthesized β-Mg_2CoH_5 by MM of the 2Mg–Co mixture with the subsequent sintering at 350 °C under 5.0 MPa of hydrogen pressure for one day, and obtained a yield of 30%. In our group, a higher yield of β-Mg_2CoH_5 was achieved by using MM of the 2Mg–Co mixture during 200 h followed by sintering at 410 °C under 6.0 MPa hydrogen pressure [10]. Mg_2CoH_5 hydride was observed after only 20 h, obtaining in this case a yield of 65%. Later on, we studied the influence of sintering parameters (pressure, temperature, time) in the formation of different hydrides in the Mg–Co–H system. Using MM under argon followed by sintering at 425 °C and 5.9 MPa of hydrogen pressure, an 89% of Mg_2CoH_5 was obtained [11]. The improvement in the performance of this synthesis procedure was attributed to the microstructural modifications introduced during the previous milling step under argon. In a recent research, Norek et al. obtained the hydride Mg_2CoH_5 by MM of MgH_2–Co mixture and subsequent sintering at high hydrogen pressure (>8.5 MPa) [12]. The ternary hydride is formed in less than 2.5 h with an average yield of 90% at a temperature of 300 °C.

Aiming at avoiding the drastic experimental conditions used during sintering, an important improvement in the preparation of hydrides was achieved by RMM. With this technique, the raw materials are ground under hydrogen pressure (up to 1.0 MPa) at room temperature to favor a gas–solid reaction during milling, creating structural/surface defects and producing the refinement of the material. In this way, Chen et al. [13] synthesized β-Mg_2CoH_5 by RMM of a mixture of $2MgH_2$–Co (one-step process). According to experimental evidence, the yield of hydride seemed to be high (as regards pressure–composition isotherms) but its exact value was not informed. Similarly, Rongeat et al. [14] produced β-Mg_2CoH_5 by RMM of the 2 Mg–Co mixture to determine thermodynamic properties by HP-DSC measurements. Again, the Mg_2CoH_5 yield was not reported. Among all the studies developed by our group on the Mg–Co–H system, Gennari and Castro [8] were the first applying RMM to the 2Mg-Co mixture, with a yield of 20% of β-Mg_2CoH_5. In a later trial, within our group González et al. [10,15] performed the synthesis of $Mg_6Co_2H_{11}$ and Mg_2CoH_5, introducing a previous step to the RMM and/or sintering step, which consisted of pre-milling the 2Mg–Co mixtures under argon. It was possible to produce Mg_2CoH_5 from MM of the 2Mg–Co mixtures followed by RMM (0.5 MPa of hydrogen pressure), achieving a yield of 50% after 90 h milling [15]. In a recent research, Zhang et al. [16] carried out the synthesis of Mg_2FeH_6, Mg_2CoH_5 and Mg_2NiH_4 by RMM using mixtures of 2Mg-TM (TM = Fe, Co, Ni) under 7.5 MPa of hydrogen pressure. The synthesis was performed for reaction periods of ~240 min (4 h) without an incubation phase and with yields of ~80% for each complex hydride [16]. The analysis of *in situ* hydrogen absorption curves showed that the synthesis of the complex hydrides followed the reaction pathway and was preceded in all cases by the formation of the MgH_2 phase.

Taking into account the mild conditions involved during RMM and that the MgH_2 is an intermediate phase during the formation of Mg_2CoH_5, the current work explores the synthesis of Mg_2CoH_5 and $Mg_6Co_2H_{11}$ complex hydrides by RMM of the 2:1 and 3:1 MgH_2–Co mixtures. The kinetic of hydrogen absorption/desorption of the final product of the RMM was studied on the basis of its potential application for hydrogen storage. The analysis of the hydride phases formed at different kinetic conditions allows an understanding of the interactions that occur in the Mg–Co–H system at different temperatures after cycling.

2. Experimental

For the synthesis, magnesium hydride (MgH_2, purity higher than 98%) and metallic cobalt particles (Co, purity higher than 99.9%) were purchased at Sigma–Aldrich. The MgH_2–Co mixtures with 2:1 and 3:1 relative composition were milled with a Frisch P6 planetary mill under 0.5 MPa of hydrogen atmosphere during different periods of time. The experimental conditions were 400 rpm, with a ball to-powder weight ratio of 80:1. All materials were handled in an argon–filled glove box, with moisture and oxygen levels kept below 1 ppm.

The samples were milled for a total time of 5 h. At regular intervals, small amounts of powder were taken out for analysis and the container was refilled with hydrogen after every extraction in order to keep the hydrogen pressure constant. To identify different phases, crystalline structure of samples was determined by powder X-ray diffraction (PXRD Philips PW 1710/01 Instruments) with CuKα radiation (graphite monochromator). During the PXRD data collection all the samples were maintained under argon atmosphere by using a tightly sealed sample holder to avoid oxidizing and decomposition. Crystallite sizes were estimated from PXRD peaks by the Scherrer equation. The thermal behavior of the samples was investigated by differential scanning calorimetry (DSC, TA 2910 calorimeter) using a heating rate of 5 °C min^{-1} and an argon flow of 122 ml min^{-1}. In order to evaluate the amount of hydride phase in the target sample, both DSC and hydrogen desorption profiles were measured to determine the endothermic heat due to hydrogen desorption and the amount of desorbed hydrogen, respectively. The proportion of Mg_2CoH_5 was calculated from the DSC curves, using the peak area and the reported value of about 82 kJ mol^{-1} for the decomposition heat of Mg_2CoH_5 [2,6]. The DSC cell constant was determined using MgH_2 as a reference sample because its decomposition enthalpy is well known. Microstructural characterizations were performed by transmission electron microscopy (TEM Philips CM200 UT operating at 200 kV). To minimize the exposition to air and moisture, the hydrided powders were placed inside a plastic vial under argon before taking them out from the glove box. Samples for TEM were prepared by spreading a small amount of powder in hexane and adding a drop of the suspension obtained on a commercial holey carbon coated gold grid.

Isothermal hydrogen sorption measurements were performed by using a modified Sieverts-type device, coupled with a mass flow controller. Hydrogen absorption/desorption rates were evaluated between 250 and 300 °C under 5.0/0.02 MPa of hydrogen pressure. Kinetic measurements were carried out after two successive cycles of hydrogen absorption/desorption at 350 °C, to ensure stabilization of the materials and reproducibility in the measurements. No activation was necessary on the samples. After the stabilization, successive hydriding/dehydriding cycles at a fixed temperature were measured and a representative kinetic behavior after 20–30 cycles was observed.

3. Results and discussion

3.1. *Synthesis of Mg–Co–H hydrides from RMM*

Aiming at synthesizing both Mg_2CoH_5 and $Mg_6Co_2H_{11}$ complex hydrides within the Mg–Co–H system, we performed the RMM of the $2MgH_2$–Co and $3MgH_2$–Co mixtures. We expected to obtain Mg_2CoH_5 and $Mg_6Co_2H_{11}$ from the $2MgH_2$–Co and $3MgH_2$–Co mixtures, respectively. However, to our knowledge, there are no previous reports on the synthesis of $Mg_6Co_2H_{11}$ by MM or RMM.

Fig. 1 shows PXRD patterns of the $2MgH_2$–Co mixture after RMM as a function of milling time. The incipient formation of Mg_2CoH_5 is clearly detected after 1 h of milling, with a simultaneous appearance of γ-MgH_2 [17]. This phase is a metastable high-pressure structure of MgH_2 [18] and it is formed due to a high plastic deformation of the phase during milling [17]. At this milling time, both starting β-MgH_2 and Co phases are also identified. RMM up to 2.5 h conduces to practically complete consumption of MgH_2 (β and γ phases) and Co, with a simultaneous formation of additional amounts of Mg_2CoH_5. Minimal changes are detected after extra 2.5 h of milling, noticing a decrease in the most intense peaks of Co. No peaks corresponding to any of the MgH_2 phases are detected after 5 h of milling. Thus, we conclude that the RMM of the $2MgH_2$–Co mixture for 5 h produces Mg_2CoH_5 as the main crystalline phase. The crystallite size of the Mg_2CoH_5 synthesized is 18 nm, indicating a high degree of refinement reached as a consequence of RMM. The global reaction of RMM can be expressed as:

$$2MgH_2(s) + Co(s) + \frac{1}{2}H_2(g) \rightarrow Mg_2CoH_5(s) \quad (1)$$

To analyze the thermal stability of the $2MgH_2$–Co mixture as a function of the reactive milling time, DSC curves are shown in Fig. 2. As a general behavior, a sharp endothermic peak is identified and associated with the hydrogen desorption from the sample. PXRD analysis performed on the samples after DSC runs confirms the complete MgH_2 and/or Mg_2CoH_5 decomposition, depending on the starting phases (not shown). After 1 h of RMM the endothermic peak at 325 °C is mainly due to the hydrogen desorption of the MgH_2. This temperature is lower than that reported for MgH_2 milled under similar conditions, due to the catalytic role of Co [19]. As milling time increases, the endothermic peaks progressively shift towards higher temperatures, from 325 °C to 349 °C. This behavior could be associated with the progressive formation of Mg_2CoH_5. Thus, it can be inferred that the longer Mg_2CoH_5 formation during RMM, the higher the hydrogen desorption temperature becomes (see Fig. 1). Similar results were observed during the RMM of 2Mg–Co mixture [15]. As milling time increase, MgH_2 disappears while Mg_2CoH_5 is progressively formed and, consequently the hydrogen desorption peak shifts to higher temperature. Finally, the endothermic peak located at 349 °C is ascribed to Mg_2CoH_5 decomposition, with a procedure yield of 83% (assuming a $\Delta H \approx 82$ kJ/mol H_2). The yield was also verified using volumetric hydrogen desorption, obtaining 3.8 wt% of hydrogen released (theoretical value 4.4 wt%). It is interesting to mention that the expected endothermic peak near 210 °C associated with tetragonal to cubic transition of Mg_2CoH_5, was not clearly observed. Similar results were previously obtained from Mg_2CoH_5 powders synthesized by RMM [8,15]. Probably, the microstructural characteristics of Mg_2CoH_5 produced by RMM (nanometric grain sizes) difficult the detection of the phase transition.

Fig. 3 displays the PXRD patterns of the $3MgH_2$–Co mixture after RMM as a function of milling time. After 0.5 h of milling, both starting β-MgH_2 and Co phases are identified as well as the formation of metastable γ-MgH_2 phase [18]. As happens during RMM of the $2MgH_2$–Co mixture (Fig. 1), the milling of the $3MgH_2$–Co mixture leads to the early formation of Mg_2CoH_5. The intensity of the peaks of Mg_2CoH_5 increases

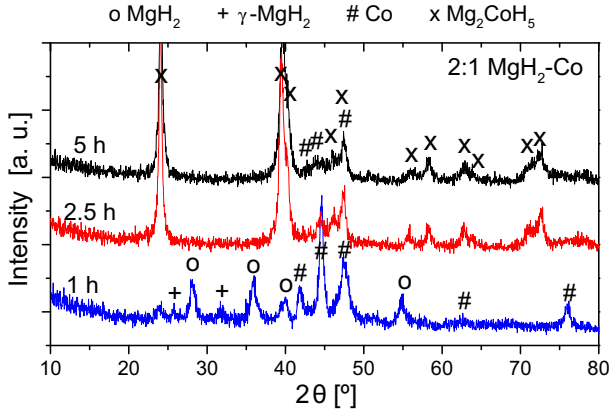

Fig. 1 – PXRD patterns of the $2MgH_2$–Co mixture after RMM for different times: (a) 1 h, (b) 2.5 h, (c) 5 h.

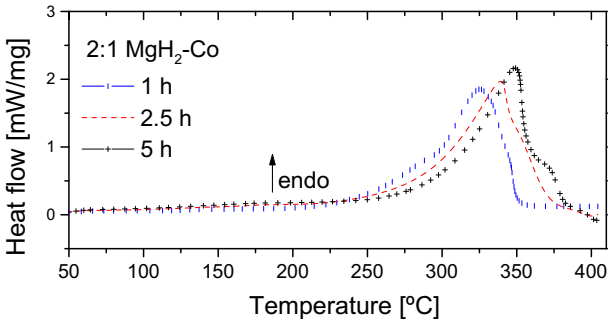

Fig. 2 – DSC curves of the $2MgH_2$–Co mixture after RMM for different times: (a) 1 h, (b) 2.5 h, (c) 5 h.

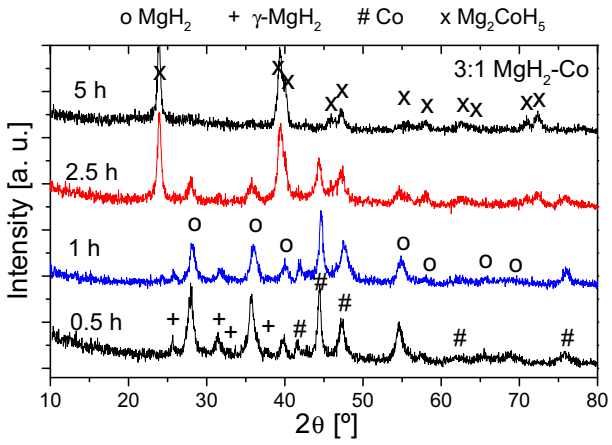

Fig. 3 – PXRD patterns of the $2MgH_2$–Co mixture after RMM for different times: (a) 0.5 h, (b) 1 h, (c) 2.5 h, (d) 5 h.

with milling progress and become wider due to defect density growth and crystallite size reduction (up to 20 nm). Milling for 2.5 h reduces noticeably the relative amounts of MgH_2 (β and γ phases) and Co phases yielding Mg_2CoH_5. After 5 h of RMM, practically the only crystalline phase is Mg_2CoH_5, whereas only two broad peaks associated with β-MgH_2 are detected. The crystallite final size of the Mg_2CoH_5 is 20 nm. Thus, the RMM of the $3MgH_2$–Co, which has the stoichiometric 3 Mg:Co ratio corresponding with $Mg_6Co_2H_{11}$, allows to synthesize Mg_2CoH_5 (with a remnant amount of MgH_2) instead of $Mg_6Co_2H_{11}$. The reaction taking place during RMM can be represented:

$$3MgH_2(s) + Co(s) + \frac{1}{2}H_2(g) \rightarrow Mg_2CoH_5(s) + MgH_{2\ \text{unreacted}}(s) \quad (2)$$

The thermal study of the $3MgH_2$–Co mixture after RMM for different periods of time is shown in Fig. 4. After 0.5 h of milling, hydrogen desorption peak at 312 °C is associated with MgH_2 decomposition (β and γ phases), the only hydride detected by XRD (Fig. 3). However, the maximum of the endothermic peak shifts towards higher temperatures as milling progresses, in correlation with an increment in the proportion of Mg_2CoH_5 in the mixture (Fig. 3). For example, after 2.5 h of milling when both MgH_2 and Mg_2CoH_5 are clearly identified, a broad endothermic peak with two possible

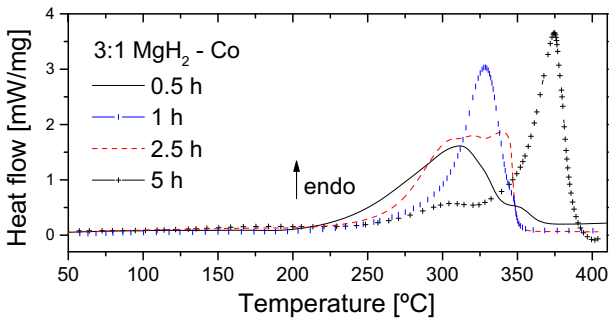

Fig. 4 – DSC curves of the $3MgH_2$–Co mixture after RMM for different times: (a) 0.5 h; (b) 1 h; (c) 2.5 h; (d) 5 h.

maxima at 323 °C and 346 °C is observed. This thermal behavior is intermediate between that of MgH_2 catalyzed by Co (Fig. 4a) and the performance of Mg_2CoH_5 (Fig. 4d). Finally, after 5 h of milling the hydrogen desorption at 374 °C is ascribed mainly to Mg_2CoH_5 decomposition, as demonstrated by XRD.

Again, no clear identification of the tetragonal to cubic phase transition of Mg_2CoH_5 was detected. The yield of Mg_2CoH_5 after 5 h of RMM is about 88%, assuming only the presence of Mg_2CoH_5 (with $\Delta H \sim 82$ kJ mol^{-1} [2,6]). In addition, volumetric measurements display that 4.8 wt% of hydrogen is obtained after RMM of $3MgH_2$–Co mixture for 5 h. Taking into account that the maximum theoretical hydrogen content is 5.0 wt% (assuming the $2Mg_2CoH_5$+MgH_2 mixture), the yield reached for reaction (2) is 96%.

As an interesting result, the thermal behavior observed after 2.5 h of RMM suggests that the decomposition of β-MgH_2 catalyzed by Co released hydrogen from the Mg_2CoH_5. This phenomenon is similar to the one observed in mixtures β-MgH_2–Mg_2NiH_4 [20] and β and γ-MgH_2 [17] obtained by RMM. This fact was ascribed to the microstructural destabilization that introduces the decomposition of the less stable phase over the one with higher stability, being both phases nanostructured and in intimate contact.

Therefore, the RMM of the MgH_2–Co mixtures with 2:1 and 3:1 ratios leads to the formation of Mg_2CoH_5, independently of the starting Mg:Co composition. Both RMM procedures conduce to high Mg_2CoH_5 yield (>80%). Taking into account that the formation of Mg_2CoH_5 requires higher hydrogen pressure than $Mg_6Co_2H_{11}$ [21], the impossibility to synthesize $Mg_6Co_2H_{11}$ could be associated with a combination of thermodynamic and kinetic factors. On the one hand, kinetic restrictions operating under the experimental conditions of the RMM could favor the formation of Mg_2CoH_5 compared to $Mg_6Co_2H_{11}$. On the other hand, $Mg_6Co_2H_{11}$ is stable in a narrow range of temperature and pressure compared to Mg_2CoH_5 [10]. Thus, it is not surprising that any of the synthesis procedures previously reported [8,9,12–14,16] conduct to the synthesis of $Mg_6Co_2H_{11}$, independently if they involve MM, RMM or the hydrogen plasma–metal reaction method [22]. In general, the $Mg_6Co_2H_{11}$ phase has been observed as intermediate during the formation of Mg_2CoH_5 at high temperatures and under hydrogen pressures [1,2,6,10,11,21].

3.2. *Kinetics performance of the Mg–Co–H hydrides produced by RMM*

To analyze the kinetic behavior of different MgH_2–Co mixtures after RMM, we measured isothermal hydrogen absorption/desorption curves between 250 and 300 °C. The kinetic measurements were carried out after stabilization of the materials, which was reached after successive absorption/desorption cycles at 350 °C and 2.0/0.02 MPa, respectively. Figs. 5 and 6 depict the hydrogen sorption rate at different temperatures of $2MgH_2$–Co and $3MgH_2$–Co mixtures after 5 h of RMM. These curves are representative of the kinetic behavior of the samples after about 30 cycles. The effect of the MgH_2:Co composition on both sorption rate and hydrogen storage capacity is clearly noticed. In the hydrogen uptake/release curves, the $3MgH_2$–Co mixtures presented higher

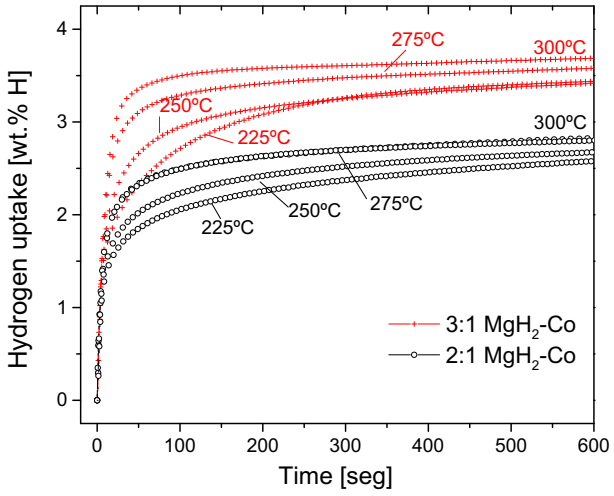

Fig. 5 – Hydrogen absorption curves at different temperatures for the $2MgH_2$–Co and $3MgH_2$–Co mixtures after 5 h of RMM. Initial hydrogen pressure = 2.0 MPa.

rates and hydrogen storage capacity than $2MgH_2$–Co mixture. As seen in Fig. 5, in 100 s $3MgH_2$–Co mixture reaches 3.5 wt% H at 300 °C (final capacity 3.7 wt% H in 10 min) and 2.9 wt% H at 250 °C (final capacity of 3.4 wt% H in 10 min). It is also seen that $2MgH_2$–Co mixture achieves 2.5 wt% H at 300 °C (final capacity of 2.8 wt% H in 10 min) and 2.2 wt% H at 250 °C (final capacity of 2.5 wt% H in 10 min).

The dehydriding curves of $3MgH_2$–Co and $2MgH_2$–Co mixtures are shown in Fig. 6. At 300 °C, $3MgH_2$–Co mixture desorbs 3.7 wt% H in 30 min, whereas $2MgH_2$–Co mixture only releases 2.6 wt% H. It is clear that the hydrogen desorption rate is practically nullified by temperature decrease. In fact at 300 and 275 °C, $3MgH_2$–Co mixtures present faster desorption rates than $2MgH_2$–Co. At 250 °C, the hydrogen release rate is the same for $3MgH_2$–Co and $2MgH_2$–Co mixtures which

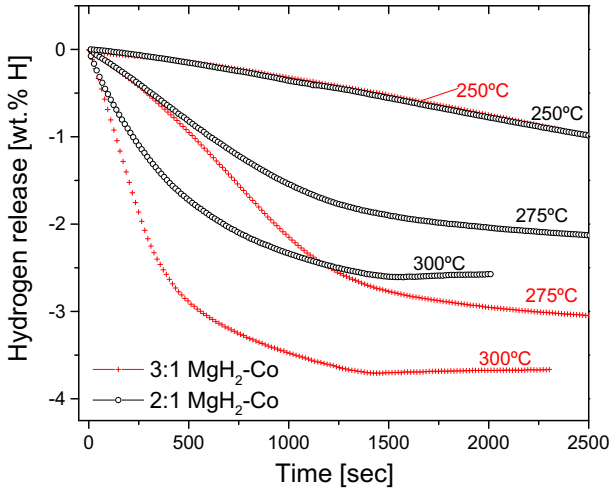

Fig. 6 – Hydrogen desorption curves at different temperatures for the $2MgH_2$–Co and $3MgH_2$–Co mixtures after 5 h of RMM. Hydrogen desorption pressure = 0.02 MPa.

suggests that a thermodynamic factor rather than a kinetic one controls the global rate.

Although the main crystalline phase is Mg_2CoH_5 after RMM of the $2MgH_2$–Co and $3MgH_2$–Co mixtures, hydrogen cycling can cause the disproportion of Mg_2CoH_5 to Mg and Co and/or the formation of other hydrides phases. To understand the kinetic behavior of the MgH_2–Co mixtures after 30 cycles of hydriding/dehydriding, we analyzed by PXRD the samples obtained after hydriding them at different temperatures (PXRD not shown). Table 1 summarizes the final phases obtained for the $2MgH_2$–Co and $3MgH_2$–Co mixtures after 30 hydrogen cycles and further hydriding. The main phases detected at 300 °C for the $2MgH_2$–Co mixture are MgH_2 and Co, with a minor amount of Mg_2CoH_5. For the $3MgH_2$–Co mixture, absorption at 300 °C leads mainly to the formation of Mg_2CoH_5 and $Mg_6Co_2H_{11}$, with the simultaneous presence of β-MgH_2 and Co. The formation of different phases depending on temperature, hydrogen pressure and the composition of the starting MgH_2–Co mixture is in agreement with our previous results [21]. In particular, at 300 °C under 2.0 MPa of hydrogen pressure, the $3MgH_2$–Co mixture provides enough amount of Mg surrounded by Co to facilitate the formation of both Mg_2CoH_5 and $Mg_6Co_2H_{11}$. However, the hydriding of the $2MgH_2$–Co mixture after cycling leads practically to the complete disproportion, obtaining mainly β-MgH_2. For the $3MgH_2$–Co mixture, when the temperature is reduced to 250 °C, the main phase is β-MgH_2 with minor amounts of Mg_2CoH_5, $Mg_6Co_2H_{11}$, Co and Mg. After hydrogen cycling, small amounts of unreacted Co are detected by PXRD (see Table 1) and associated with the cubic phase [12]. These results evidence that both reactions (1) and (2) are not completely reversible under hydrogen cycling.

The microstructure of the mixtures after RMM, hydriding/dehydriding cycling and posterior hydriding at 300 °C was observed by TEM. Figs. 7 and 8 correspond to the $2MgH_2$–Co and $3MgH_2$–Co mixtures, respectively. Different phases were identified by selected area electron diffraction (SAED) and dark field (DF) imaging. The diffraction pattern corresponding to the encircled region in the bright field image shown in Fig. 7a can be observed in the inset in Fig. 7b. The reflection indicated by an arrow corresponds to 101 of β-MgH_2, indexed as a tetragonal structure (PDF 74-0934). The dark field image using this reflection is shown in Fig. 7b and reveals the presence of β-MgH_2 crystallites inside the $2MgH_2$–Co mixture. The diffraction pattern corresponding to Fig. 8a is shown in the inset in

Table 1 – PXRD analysis performed on the $2MgH_2$–Co and $3MgH_2$–Co mixtures after hydrogen cycling and further hydriding at different temperatures.

Sample	Absorption temperature (°C)	Phases detected by PXRD*
$2MgH_2$–Co	300	**β-MgH_2**, Co, Mg_2CoH_5
$3MgH_2$–Co	300	**Mg_2CoH_5, $Mg_6Co_2H_{11}$**, Co, βMgH$_2$
$3MgH_2$–Co	250	**β-MgH_2**, Mg_2CoH_5, $Mg_6Co_2H_{11}$, Co, Mg

* The main hydride phase is indicated in bold letters.

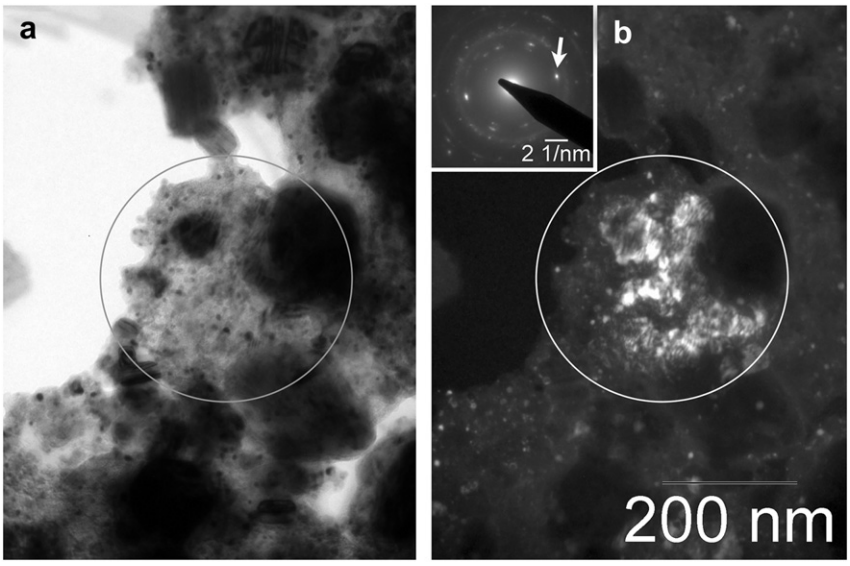

Fig. 7 – TEM images of $2MgH_2$–Co mixture after hydrogen cycling and further hydriding at 300 °C showing β-MgH_2 crystallites. a) Bright field image. b) DF image with reflection 101 of β-MgH_2 indicated in the SAED pattern (inset).

Fig. 8b. In this case, the diffraction ring indicated by an arrow was clearly identified as 111 Mg_2CoH_5, indexed as a cubic fluorite structure (PDF 78-0216). In the corresponding dark field 111 image shown in Fig. 8b, three Mg_2CoH_5 particles of about 60–100 nm can be distinguished. The β-MgH_2 and Mg_2CoH_5 phases identified by TEM in $2MgH_2$–Co and $3MgH_2$–Co mixtures, respectively, after cycling and hydriding at 300 °C correspond to main hydride phases identified by PXRD (see Table 1). Co particles were also observed in both $2MgH_2$–Co and $3MgH_2$–Co mixtures, as shown in Figs. 9 and 10 respectively. DF images, Figs. 9b and 10b, were obtained with the 111 FCC Co reflection from the $[0\bar{1}1]$ FCC Co zone axis, as shown in Fig. 10c. Even though some distortion could be detected in the diffraction pattern due to the milling process, the energy dispersive X-ray spectroscopy of the particle (EDS) shown in Fig. 10d confirms the presence of a Co phase. The FCC structure of Co was reported in [23]. The presence of a weak O intensity at 0.523 keV may be explained by oxidation of some phases during preparation and transfer of the sample to the TEM.

Therefore, on the basis of the results shown in Table 1, the hydrogen absorption curve at 300 °C for the $3MgH_2$–Co (Fig. 5) represents mainly the formation rate of the Mg_2CoH_5 and $Mg_6Co_2H_{11}$ complex hydrides. On the contrary, for the $2MgH_2$–Co mixture at the same temperature, the hydriding curve principally corresponds to the formation of MgH_2 catalyzed by Co. In our previous work, we demonstrate that the reaction $Mg(s) + H_2(g) \rightarrow MgH_2(s)$ is favored at temperatures below 300 °C, with Co acting as catalyst. Thus, the formation

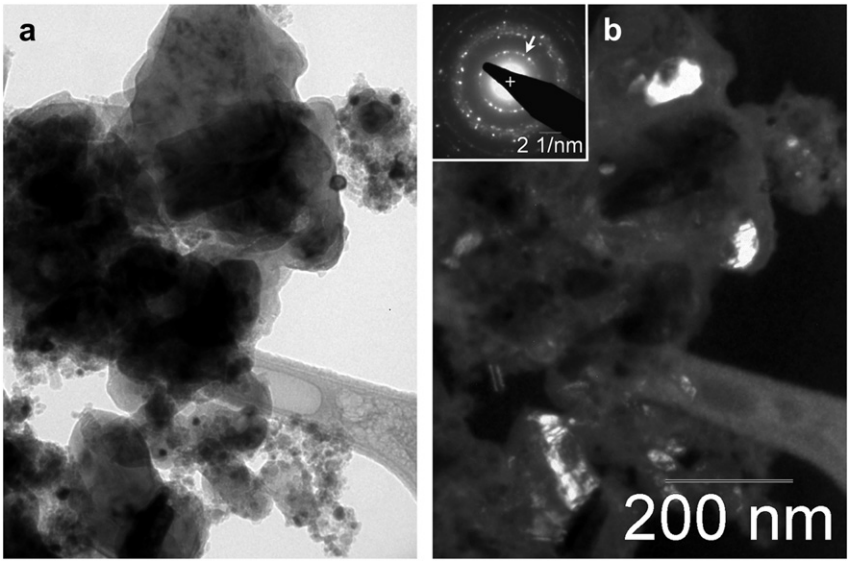

Fig. 8 – TEM image of $3MgH_2$–Co mixture after hydrogen cycling and further hydriding at 300 °C. a) Bright field image. b) DF image with reflections from the 111 Mg_2CoH_5 diffraction ring indicated in the SAED pattern (inset). Three Mg_2CoH_5 particles of about 60–100 nm can be observed.

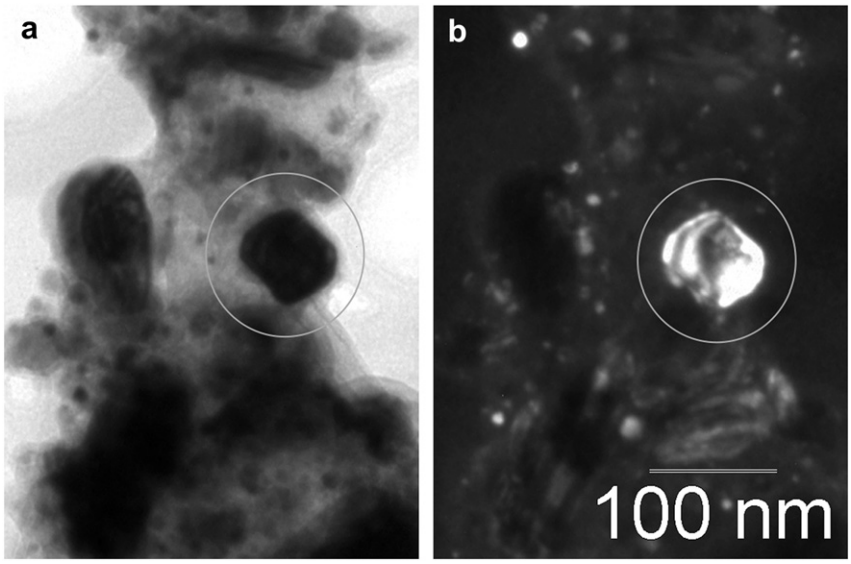

Fig. 9 – TEM image of a Co FCC particle in $2MgH_2$–Co mixture after hydrogen cycling and further hydriding at 300 °C. a) Bright field image. b) DF 111 Co FCC image.

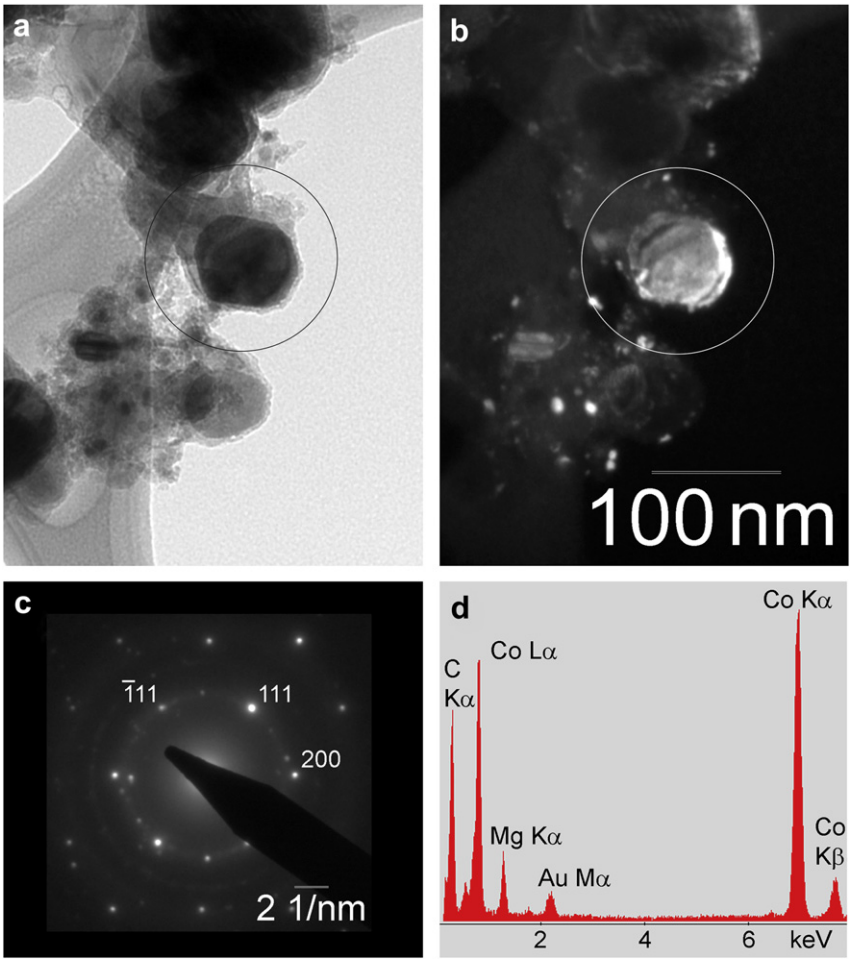

Fig. 10 – Co FCC particle in $3MgH_2$–Co mixture after hydrogen cycling and further hydriding at 300 °C. a) Bright field TEM image. b) DF 111 image. c) Corresponding indexed [$0\bar{1}1$] Co FCC zone axis diffraction pattern. d) Corresponding EDS showing the Co main intensities. X-rays from Mg of the surrounding matrix and Au and C from the grid are also contributing.

of Mg_2CoH_5 in the $3MgH_2$–Co mixture could mainly occur via reaction (1) [12], which is not completely reversible. In addition, the high hydrogen storage capacity reached for this mixture can be associated with the possibility to form Mg–Co complex hydrides (even at 250 °C). Considering that hydrogen pressure and temperature are kept constant for both 2:1 and 3:1 MgH_2–Co mixtures, the local Mg:Co composition determines which complex hydrides could be formed and it is also responsible of the hydrogen absorption/desorption behavior displayed.

4. Conclusions

Conclusions regarding the RMM of the $2MgH_2$–Co and $3MgH_2$–Co mixtures and their hydrogen storage performance are listed below:

1. The Mg_2CoH_5 complex hydride was successfully synthesized by RMM process of the $2MgH_2$–Co and $3MgH_2$–Co mixtures after only 5 h, with a yield of >80%. The synthesis procedure involves a single step and mild experimental conditions (0.5 MPa of hydrogen and room temperature).
2. The attempt to produce $Mg_6Co_2H_{11}$ by RMM of the $3MgH_2$–Co mixture was unsuccessful. Considering that $Mg_6Co_2H_{11}$ was only observed as a secondary phase during the formation of Mg_2CoH_5 at high temperatures and hydrogen pressures, the impossibility of its synthesis could be attributed to kinetic restrictions under milling conditions and/or to intrinsic thermodynamic properties of the phase.
3. Under cycling, although the hydrogen storage capacity was constant, a disproportion of the starting materials occurred. For the $3MgH_2$–Co mixture, formation of Mg_2CoH_5, $Mg_6Co_2H_{11}$ and MgH_2 in different amounts occurs depending on the temperature (between 250 and 300 °C). In the case of $2MgH_2$–Co mixture, the majority phase is MgH_2 independent of the temperature. Minor amounts of Mg_2CoH_5 are only observed at 300 °C.
4. The RMM allows the production of Mg_2CoH_5 in the nanometric range, reaching an homogeneous Mg–Co mixing degree. Hydrogen absorption/desorption cycling modifies both Mg_2CoH_5 and Co grain sizes, leads to non-uniform grain sizes and induces grain growth.
5. The best hydrogen storage material was $3MgH_2$–Co mixture, which showed high hydrogen absorption/desorption rates, good stability after cycling and adequate hydrogen storage capacities (3.7 wt% hydrogen) at temperatures between 250 and 300 °C. However, this material does not meet the technological targets for its use in mobile applications.

Acknowledgments

This study has been partially supported by CONICET (National Council of Scientific and Technological Research), CNEA (National Commission of Atomic Energy), ANPCyT (PICT No 1049) and Instituto Balseiro (University of Cuyo).

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