Reversible hydrogen storage in Mg_2CoH_5 prepared by a combined milling-sintering procedure

I. González Fernández [a], G.O. Meyer [a,b,c], F.C. Gennari [a,b,c,*]

[a] *Instituto Balseiro, U.N. Cuyo, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET, Argentina*
[c] *Centro Atómico Bariloche (CNEA), R8402AGP, S. C. de Bariloche, Argentina*

Abstract

Mg_2CoH_5 hydride was synthesized in a two step procedure: milling a 2Mg–Co mixture under inert atmosphere at room temperature followed by sintering at 410 °C under 6.0 MPa of hydrogen pressure for one week. Under these conditions hydride formation first occurs in only 20 h, which is much faster than previously reported experiments. This improvement in the synthesis procedure can be associated with better intermixing of Mg–Co and refinement of the microstructure obtained during milling stage. The microstructure, structure and thermal behavior of the phases formed during the 2Mg–Co processing were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). From a combination of XRD and DSC measurements, the transition from tetragonal to cubic structure of Mg_2CoH_5 at 203 °C and its decomposition at 390 °C with subsequent MgCo intermetallic formation were identified. Measurements of equilibrium and kinetics properties of the reaction with hydrogen were performed using modified Sieverts-type equipment. Two plateaus were identified in the absorption pressure-composition isotherms, which were associated to the formation of Mg_2CoH_5 and $Mg_6Co_2H_{11}$ hydrides. Hydrogenation and dehydrogenation reactions were reversible on cycling, with fast absorption rate in the range 250–400 °C.
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Keywords: Metal hydrides; Mechanical alloying; Kinetics

1. Introduction

The interest in the transition metal hydride Mg_2CoH_5 for hydrogen storage is based on its high storage capacity (4.5 wt%), high hydrogen volumetric density (about 100 kg H_2 m^{-3}), better hydrogen absorption/desorption kinetics than pure magnesium and low cost. However, this hydride has the peculiarity that Mg_2Co intermetallic compound has not been observed in a stable form, which difficults Mg_2CoH_5 production [1,2]. In addition, depending on the experimental conditions, two different hydrides can be observed in the Mg–Co–H system [3–7]: Mg_2CoH_5 and $Mg_6Co_2H_{11}$. The first shows a tetragonal structure at low temperature (labeled as β-phase), which transforms into a disordered cubic one at around 200 °C [3–5]. $Mg_6Co_2H_{11}$ contains two different complex anions in an orthorhombic structure (labeled γ-phase) being able to store up to 4.0 wt% of hydrogen [7].

Sintering [3,6] and different alternatives of mechanical alloying [4,8–10] were the preferred techniques for the synthesis of Mg_2CoH_5. Sintering procedure was first performed by Ivanov et al. [3] and involved pressing of a mixture of Mg–Co powders followed by a thermal treatment at 350–500 °C under hydrogen pressures of 4.0–6.0 MPa. Under these conditions, the hydride formation was not completed and the main remaining phases were MgH_2 and Co. Later on, nearly single-phase β-Mg_2CoH_5 was produced by Selvam and Yvon [6] using sintering at 9.0 MPa and 450 °C. Changes in the experimental conditions (450–500 °C and 1.5–5 MPa) conduce to the production of a mixture of β-Mg_2CoH_5 and γ-$Mg_6Co_2H_{11}$. In the case of mechanical alloying, the alternatives used to obtain Mg_2CoH_5 involved: (i) milling Mg and Co under inert atmosphere or reactive atmosphere followed by hydriding [4,8], (ii) milling Mg and Co under H_2 atmosphere (reactive mechanical alloying, RMA) [10] and (iii) milling MgH_2 and Co under H_2 atmosphere [9]. When the milling was performed starting from a Mg–Co

mixture the maximum calculated yield was about 30 wt% [8,10], while beginning with a MgH$_2$–Co mixture resulted in higher amount of hydride but it was not reported [9]. Recently, Shao et al. [11] have proposed a modification of the sintering method that involves the use of Mg and Co nanoparticles obtained by a hydrogen plasma-metal reaction (HPMR) method, followed by a temperature–pressure treatment. The yield of Mg$_2$CoH$_5$ was 97 wt% after sintering under 4.0 MPa (48 h at 350 °C or 1 h at 400 °C).

In the present work Mg$_2$CoH$_5$ was successfully prepared from Mg and Co powders milled under Ar atmosphere to obtain a nanoscale mixture of the metals, followed by conventional sintering procedure (410 °C and 6.0 MPa). Pressure–composition isotherms (PCI) and hydrogen absorption/desorption curves were obtained to characterize the material.

2. Experimental

Elemental powders of Mg and Co (purity higher than 99%) were mechanically milled under argon atmosphere using a Uni-Ball-Mill II apparatus (Australian Scientific Instruments). Powders with a 2Mg–Co ratio and ferromagnetic steel balls were placed in a stainless steel container, closed within an Ar dry box and milled under Ar atmosphere during 200 h. A portion of the as-milled sample (0.5 g) was pressed under 3 t to obtain a cylindrical pellet that was used as starting material for the synthesis of Mg$_2$CoH$_5$ by sintering [3,6]. Based on previous results, the pellet was kept under 6.0 MPa of hydrogen pressure at 410 °C for seven days.

Sintering procedure was performed in a modified Sieverts device [12] where the system pressure can be precisely set operating a mass flow controller. Hydrogen pressure, reactor temperature and room temperature were all monitored and the first automatically controlled by the software designed for this experiment. If reactor pressure dropped from 6.0 MPa more than 0.01 MPa because of sample absorption, hydrogen pressure was set again in its set point value by a programmed opening of the mass flow controller.

The crystalline structure of samples was characterized by X-ray diffraction (XRD) on a Philips PW 1710/01 instrument with Cu Kα radiation (graphite monochromator). Strain and crystallite size effects were estimated from diffraction peaks using a Gauss–Lorentz component. Mg–Co distribution was studied by scanning electron microscopy (SEM 515, Philips Electronic Instruments) on resin-mounted and polished samples. The thermal behavior was investigated by differential scanning calorimetry (DSC, TA 2910 calorimeter) using a heating rate of 5 °C min^{-1} and an Ar flow of 122 ml min^{-1}. The proportion of Mg$_2$CoH$_5$ was calculated from the DSC curves, using the peak area and the reported value of 86 kJ mol^{-1} for the formation heat of Mg$_2$CoH$_5$ [4].

Same equipment used for hydride synthesis allowed performing dynamic pressure–composition isotherms (PCI) and hydrogen absorption/desorption curves [12]. The sample was heated up to the reaction temperature under vacuum and kept at this temperature for 30 min before beginning each hydrogen absorption measurement.

3. Results and discussion

Fig. 1 (A and B) show the XRD patterns of the 2Mg–Co mixture after milling during 2 and 200 h, respectively. The sample milled during 200 h did not produce reflections of new phases such as Mg–Co compounds or MgO. The main changes were the reduction in the reflection intensity and the broadening of Mg peaks (JCPDS Powder Diffraction Data Card No 35-0821), both being signals of grain refinement. The Mg crystallite size was reduced from 140 to 10 nm, with an increment in the material strain. In the case of Co (JCPDS Powder Diffraction Data Card No 5-0727) its reflections were slightly affected after the same
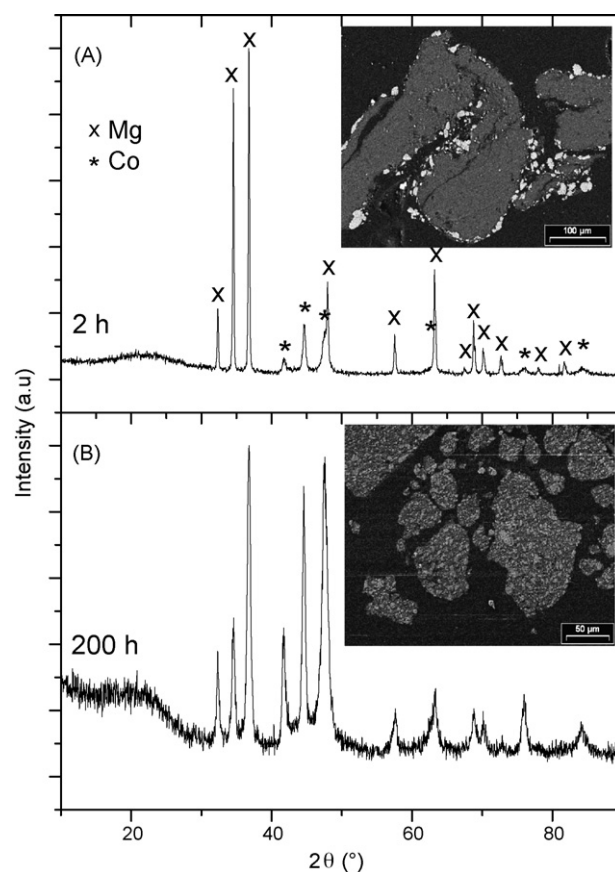

Fig. 1. X-ray diffraction patterns and SEM backscattered electron images of the 2Mg–Co mixture after: (A) 2 h and (B) 200 h of milling. (×) Mg, (*) Co.

milling time. The starting crystallite size was reduced to about 10 nm. The distribution of Mg and Co phases was observed with backscattered electrons (inset picture in Fig. 1). The bright phase corresponds to Co while the dark one to Mg. After milling for 2 h, Co particles were hardly incorporated into the Mg matrix with lamellar like morphology. Repeated flattening, fracturing and welding up to 200 h reduced the agglomerate size distribution, producing the refinement of the microstructure that favored the homogeneous dispersion of the Co particles within the Mg matrix.

The as-milled sample was pressed to form a pellet and put it into the reactor as starting material for the Mg$_2$CoH$_5$ synthesis, following the method reported in [3,6] (see Section 2). The rate of the initial hydrogen absorption is shown in Fig. 2A. A striking result is that most hydrogen consumption occurred during the first 20 h without further hydrogen absorption up to seven days. XRD pattern obtained after sintering (Fig. 2B) showed that Mg$_2$CoH$_5$ was the main phase (JCPDS Powder Diffraction Data Card No 44-1160). Some minor peaks were indexed as Co and MgH$_2$ (JCPDS Powder Diffraction Data Card No 5-0727 and No 12-0697, respectively). Both the initial hydrogen absorption curve as well as the formation of Mg$_2$CoH$_5$ in only 20 h have not been reported before. Previous works have shown that if the synthesis procedure involves Mg–Co mixing-sintering steps or milling-sintering steps, the hydrogen absorption is observed after several days [3,6], two to three days [4] or one day [8].
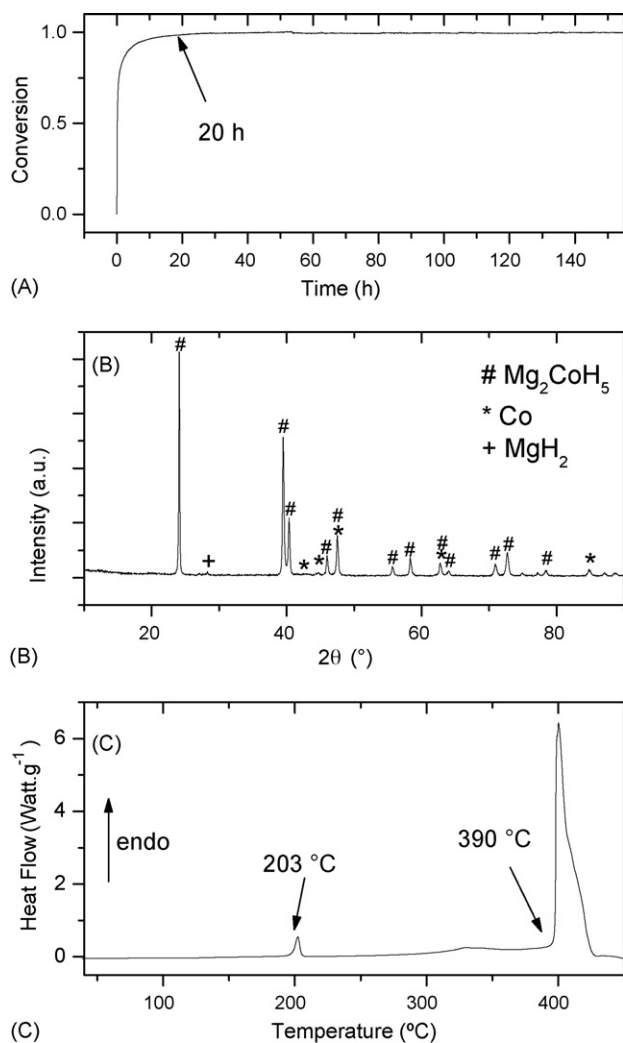
Fig. 2. (A) Hydrogen absorption rate of the 2Mg–Co milled during sintering procedure (410 °C, 6.0 MPa, seven days). (B) XRD of the 2Mg–Co milled after sintering procedure. (C) DSC curve of the Mg_2CoH_5 obtained in (A).

Fig. 3. *P–C* isotherm at 400 °C of 2Mg–Co milled after sintering procedure.

The thermal behavior of the Mg_2CoH_5, synthesized as mentioned before, is shown in Fig. 2C. The DSC curve presents two endothermic events: a small one at 203 °C due to the tetragonal to cubic structure transformation of Mg_2CoH_5 and another at 390 °C associated with hydride decomposition, as it was verified by XRD analysis after DSC measurement finished. This XRD also shows the formation of MgCo as the main phase (JCPDS Powder Diffraction Data Card No 44-1149) simultaneously with Mg and Co, in agreement with previous work [10]. It must be remarked that the temperature of the beginning of hydride decomposition is high (390 °C) in comparison with that obtained from decomposition of Mg_2CoH_5 produced by reactive mechanical alloying (300 °C) [10]. From the second endothermic event, the amount of Mg_2CoH_5 produced by milling-sintering procedure was calculated as 65 wt%. Additional work is being developed to clarify the role of the synthesis procedure on the thermal stability of the hydride and the hydride production yield. The information shown in Fig. 2A is a clear evidence of the improved reactivity of the as-milled sample in comparison with previous works [3,4,8] which can be associated
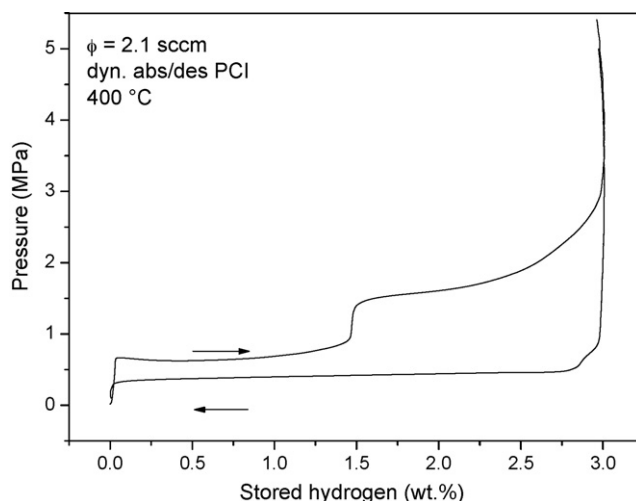
with microstructure refinement and improved Mg–Co mixing reached after 200 h of milling (Fig. 1B).

Fig. 3 shows dynamics absorption and desorption PCIs at 400 °C of as-synthesized Mg_2CoH_5. Final hydrogen storage of up to 3.0 wt% occurred in two stages given by well-defined plateaus: a flat one at 0.67 MPa and a sloped one developed between 1.6 and 3.0 MPa. On the contrary, during desorption only one plateau can be identify at about 0.4 MPa, evidencing a strong hysteresis during hydrogen absorption/desorption process. A remarkable result is the good absorption capacity observed in the first cycle, after desorption of Mg_2CoH_5 prepared by the milling-sintering process. Before this work, only Chen et al. [9] reported absorption PCI at 400 °C. They also observed two plateaus, associated to MgH_2 (low pressure) and Mg_2CoH_5 (high pressure). In our case, XRD analysis allows us to associate each plateau with the formation of Mg_2CoH_5 and $Mg_6Co_2H_{11}$ hydrides. Regarding desorption PCI there is some agreement about the existence of two plateaus related with Mg_2CoH_5 and $Mg_6Co_2H_{11}$ decomposition. We could not distinguish the contribution of each hydride decomposition.

Although many research papers analyzed the thermodynamics of the Mg_2CoH_5 [3,4,9,11,13] only one work characterized the hydrogen absorption behavior [11]. Fig. 4 (A and B) show hydrogen absorption/desorption reactions at 250 and 300 °C for the Mg_2CoH_5 produced by milling-sintering. Hydrogen absorption proceeded fast at both temperatures, storing about 2 wt% in only two minutes. Hydride decomposition was practically non-detectable at 250 °C in agreement with DSC measurement (Fig. 2B), whereas 5 h were needed to desorb 1.7 wt% at 300 °C. Absorption rates of our samples were faster than those reported for Mg_2CoH_5 produced by HPMR (nanoparticles of Mg and Co) followed by sintering [11]. No desorption data are available to compare with the results obtained in this work. The reported curves here correspond to the cycle number 25 (300 °C) and 28 (250 °C). The full analysis of all curves (not shown) allows to state that hydrogen sorption shows reversibility after 50 cycles, without loss of the hydrogen storage capacity and good sorption rate at 300 °C.
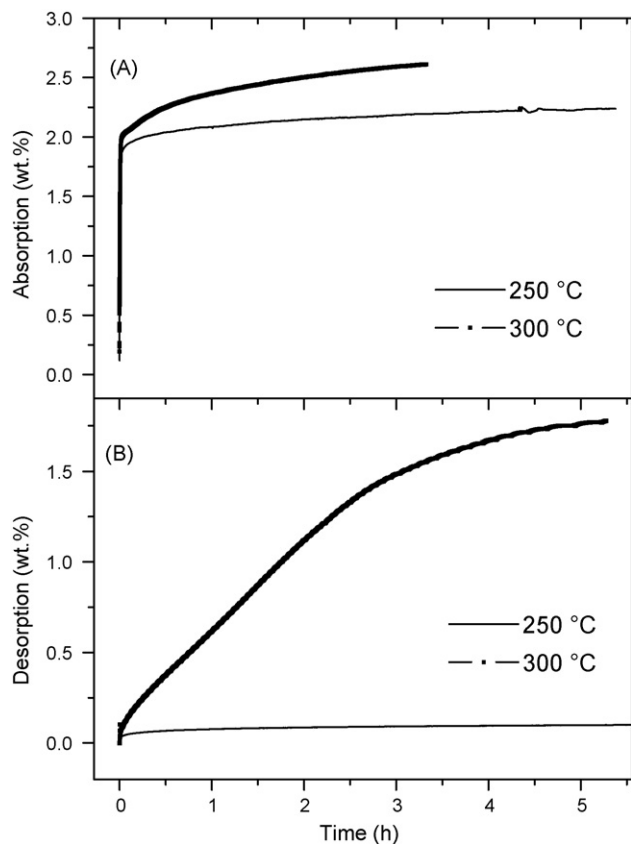
In particular, hydride production yield of about 30 wt% was obtained with another milling/sintering procedure [8]. Analysis of SEM and XRD data indicated that the improvement in the synthesis procedure can be related with the nano-distribution of Mg–Co previous to the sintering stage.

Absorption PCI at 400 °C showed two plateaus, which can be associated to the formation of Mg_2CoH_5 and $Mg_6Co_2H_{11}$ hydrides. Hydrogenation/dehydrogenation properties of as-synthesized Mg_2CoH_5 showed good reversibility on cycling. The absorption rate was fast at temperatures as low as 250 °C, storing 2 wt% in only two minutes. The improvement in the synthesis procedure of Mg_2CoH_5, the reversibility observed on cycling and the fast hydrogen absorption rate are promissory results for the potential use of this material for hydrogen storage.

Acknowledgements

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Fig. 4. Hydrogen (A) absorption and (B) desorption curves at 250 and 300 °C, of the 2Mg–Co milled after several cycles.

4. Conclusions

An alternative synthesis procedure for the production of Mg_2CoH_5 was presented. The proposed methodology introduced a modification to the conventional sintering process, including a previous stage where the 2Mg–Co mixture was milled during 200 h under Ar atmosphere. When the product of milling was pressed and heated at 410 °C and 6.0 of hydrogen pressure, the formation of Mg_2CoH_5 was observed after only 20 h. In this way, this milling-sintering procedure successfully produced Mg_2CoH_5 with higher yield (65 wt%) than those reported before, in which sintering or milling had been used.