



Thermodynamic behavior of the Mg–Co–H system: The effect of hydrogen cycling



M.G. Verón*, F.C. Gennari

Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET Instituto Balseiro, U.N. Cuyo, Argentina
Centro Atómico Bariloche (CNEA), R8402AGP, S.C. de Bariloche, Río Negro, Argentina

ARTICLE INFO

Article history:

Received 23 April 2014

Received in revised form 6 June 2014

Accepted 16 June 2014

Available online 24 June 2014

Keywords:

Hydrogen absorbing materials

Metal hydrides

Thermodynamic properties

Hydrogen storage

ABSTRACT

Thermodynamic properties of the Mg–Co–H system were investigated using equilibrium pressure measurements. Experimental determination of absorption and desorption pressure-composition isotherms (PICs) was carried out in the temperature range of 250–425 °C, using as starting material a 2Mg–Co mixture milled under argon and Mg₂CoH₅ produced by reactive ball milling of the 2MgH₂–Co mixture. It was found that the cycling affects the PICs shape and the total hydrogen storage capacity. XRPD analysis of the samples at different stage of the absorption PICs reveals that the plateau at low hydrogen pressure is associated with the formation of Mg₆Co₂H₁₁ and the plateau at higher hydrogen pressure corresponds to Mg₂CoH₅ formation. In addition, an intermediate plateau is also observed at 300 and 350 °C, which was related with the formation of MgH₂ from MgCo intermetallic.

© 2014 Published by Elsevier B.V.

1. Introduction

Transition metal complex hydrides of the family Mg_xTH_y (T = Fe, Co, Ni) are attractive materials for hydrogen storage because of their high theoretical gravimetric capacities (5.5 wt%, 4.5 wt% and 3.6 wt%, respectively), high volumetric densities of hydrogen (between 80 and 150 kg H₂ m⁻³) and low cost. In particular, the system Mg–Co–H is interesting not only for the different hydrides phases that can be observed as a function of pressure and temperature (Mg₂CoH₅, Mg₆Co₂H₁₁ and MgH₂), but also from the technological point of view by the potential kinetic/thermodynamic properties associated with these hydrides. However, the absence of stable precursors such as Mg₂Co or Mg₃Co and the simultaneous formation of MgH₂ in certain conditions of pressure and temperature make the synthesis of a complex Mg–Co hydride as a single phase from elemental Mg and Co difficult. Thus, kinetics and thermodynamic studies about Mg–Co–H system are sensitive to synthesis procedure of the starting sample, thermal treatment received (time and temperature) and pressure of hydrogen atmosphere.

Several investigations were developed to study the thermodynamics of the Mg–Co–H system [1–9]. Table 1 summarizes the

nature of the hydride phase formed as well as the enthalpy and entropy of the absorption/desorption calculated from the van't Hoff equation. The pioneering works associated with Mg₂CoH₅ and Mg₆Co₂H₁₁ hydrides are those of Zolliker, Ivanov, Konstantchuk and collaborators [1–3], which were carried on in the years 1985–1988. They reported the formation of Mg₂CoH₅ for the first time by sintering a pressed 2Mg–Co mixture at 350–500 °C under 4–6 MPa of hydrogen for several days. Pressure-composition isotherms (PICs) of this hydrided sample were measured in the temperature range from 347 to 447 °C [1,2]. The authors observed two plateaus and attribute the higher pressure one to MgH₂ and the low pressure one to Mg₂CoH₅. The estimated values of formation and dissociation enthalpies for Mg₂CoH₅ were $\Delta H = -60$ kJ/mol of H₂ and $\Delta H = -86$ kJ/mol of H₂. In a further work [3], desorption PICs were performed for the 2Mg–Co mixture previously hydrided at 387 °C under 4 MPa hydrogen pressure. From these measurements, three plateaus were obtained. The upper one corresponds to the decomposition of MgH₂, whose enthalpy and entropy values (see Table 1) are in agreement with the values reported by Stampfer for MgH₂ [4]. Enthalpies obtained from plateaus at intermediate and lower pressures were $\Delta H = -79$ kJ/mol and $\Delta H = -70$ kJ/mol of H₂ and they were associated with Mg₂CoH₅ and Mg₆Co₂H₁₁ decomposition, respectively [3].

In 1993, Yoshida and colleagues [5] using a thermobalance performed desorption PCI measurements from Mg–Co mixtures and observed one (378–398 °C) or two (>400 °C) plateaus depending on the temperature. Hydrides were not identified but

* Corresponding author at: Av. Bustillo 9500, Centro Atómico Bariloche, R8402 AGP – S.C. de Bariloche, Río Negro, Argentina. Tel.: +54 2944 445197; fax: +54 2944 445190.

E-mail address: María.gisela.veron@cab.cnea.gov.ar (M.G. Verón).

Table 1
Summary of thermodynamic data for the Mg–Co–H hydrides reported in the literature.

References	Temperature range (°C)	Phases identified	ΔH (kJ/mol)		ΔS (J/K mol)	
			Absorption	Desorption	Absorption	Desorption
Zolliker et al. [1]	347–447	MgH ₂ Mg ₂ CoH ₅	– –60 ± 5	– –86 ± 5	– –	– –
Ivanov et al. [3]	343–450	MgH ₂ Mg ₂ CoH ₅ Mg ₆ Co ₂ H ₁₁	– – –	–75 ± 1 –79 ± 4 –70 ± 4	– – –	135 ± 2 134 ± 4 118 ± 4
Yoshida et al. [5]	378–450	High pressure plateau ^a Low pressure plateau ^a	– –	–108 ± 3 –95 ± 5	– –	– –
Reiser et al. [6]	440–486	High pressure plateau ^a Low pressure plateau ^a	– –	–76 ± 4 –	– –	– –
Chen et al. [7]	280–380	MgH ₂ Mg ₂ CoH ₅	–68.4 –69.5	–74.5 –83.2	124.2 129.6	134 146.7
Shao et al. [8]	375–447	Mg ₂ CoH ₅ Mg ₃ CoH ₅	– –	–82.27 –73.16	– –	138.8 123
González et al. [9]	Abs.:350–450 Des.:400–450	Mg ₂ CoH ₅ Mg ₆ Co ₂ H ₁₁	–60 ± 2 –62.9 ± 0.8	–54 ± 8 –65 ± 2	112 ± 3 110 ± 2	99 ± 12 109 ± 3

^a Hydride phase associated with this plateau was not identified in the reference.

decomposition enthalpies of $\Delta H = -95$ kJ/mol H₂ and $\Delta H = -108$ kJ/mol H₂ were estimated for the high and low pressure plateau, respectively [5]. On the other hand, Reiser et al. performed an extended cyclic-stability test with a 2Mg–Co mixture and after that desorption PCI measurements were measured [6]. They found a plateau in the range of hydrogen content up to 2.5 wt%, which corresponds to a heat of desorption of $\Delta H = -76$ kJ/mol H₂ ± 4 kJ/mol. From there up to about 3.7 wt%, a second variable plateau was observed, but in this region no reliable value for the heat of formation was calculated [6].

Aiming to study absorption/desorption properties from a single Mg–Co hydride, new synthesis procedures were developed [7–9]. Chen et al. synthesized Mg₂CoH₅ (with high yield) by direct ball milling of 2MgH₂–Co mixture under hydrogen atmosphere and investigated its thermodynamic properties [7]. The dissociation and formation enthalpies of Mg₂CoH₅ were $\Delta H = -83.2$ kJ/mol H₂ and $-\Delta H = 69.5$ kJ/mol H₂, respectively, consistently with data reported by Zolliker et al. [1] (see Table 1). In a posterior work, Shao et al. prepared nanostructured Mg₂CoH₅ from Mg and Co nanoparticles produced by HPMR (hydrogen plasma metal reaction) method and further treatment at 400 °C at 0.4 MPa during 24 h [8]. Desorption PCI curves between 375 and 450 °C show two plateaus the low pressure one corresponding to Mg₃CoH₅ (i.e. Mg₆Co₂H₁₁) and the high pressure one to Mg₂CoH₅. The enthalpy and entropy values of decomposition calculated were $\Delta H = -82.27$ kJ/mol (–73.16 kJ/mol) and $\Delta S = -138.8$ J/K mol (–123 J/K mol) for Mg₂CoH₅ (Mg₃CoH₅) [8]. Later, González et al. obtained the Mg₂CoH₅ and Mg₆Co₂H₁₁ ternary hydrides by a combined technique that included ball milling of a 2Mg–Co mixture under Ar followed by sintering in hydrogen atmosphere [9]. They calculated the enthalpies of formation (decomposition) as $\Delta H = -62.9 \pm 0.8$ kJ/mol (–65 ± 2 kJ/mol) for Mg₆Co₂H₁₁ and $\Delta H = -60 \pm 2$ kJ/mol (–54 ± 8 kJ/mol) for Mg₂CoH₅, respectively. The desorption enthalpies obtained in this work were lower than previously reported values (Table 1). Moreover, in contrast with these thermodynamic studies performed with a sample consisting mainly Mg₂CoH₅ phase [7–9], no synthesis procedure was successfully developed up today to produce Mg₆Co₂H₁₁ as a majority hydride phase [10]. Due to this, the available formation enthalpy values for Mg₆Co₂H₁₁ are scarce.

Previous investigations [1–9] evidence that the thermodynamic data reported for the Mg–Co–H system are dependent of both the nature of the starting sample as well as its thermal history. In fact,

it is not clear from the literature the effect of the hydrogen cycling on the nature of the hydrides formed under equilibrium conditions. Evidently, the reasons for the change in the capacity and in the shape of the plateaus are not well understood. In this work the influence of hydrogen cycling on the thermodynamic behavior of 2Mg–Co mixture is analyzed. Several PCIs were performed from as-milled and as-cycled 2Mg–Co mixture and van't Hoff diagrams for Mg₂CoH₅ and Mg₆Co₂H₁₁ formation/decomposition were deduced. Significant thermodynamic properties of the Mg–Co–H system were obtained from this study and compared to previously reported information.

2. Experimental

The starting materials were commercial reagents: Mg (Riedel de Haen, 99%), MgH₂ (Aldrich, >98%) and Co (Aldrich Chem., 99.9 + %). The 2Mg:Co mixture was milled in a Uni-Ball-Mill II apparatus (Australian Scientific Instruments) under Ar atmosphere during 200 h. The experimental conditions were 200 rpm, with a ball to-powder weight ratio of 44:1. The final sample is hereafter indicated as 2M. After 200 h of milling, 2M sample consists of Mg and Co phases with crystallite sizes of 10 and 15 nm, respectively [11]. For comparison purposes, nanostructured Mg₂CoH₅ (~18 nm) was successfully synthesized by reactive mechanical milling (RMM) process, achieving a yield of >80% [10]. The synthesis involved the milling of the 2MgH₂–Co mixture with a Frisch P6 planetary mill under 0.5 MPa of hydrogen atmosphere for 5 h (sample labeled 2MH). 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.

A modified Sieverts-type device coupled with mass flow controllers was used to perform thermodynamic characterization [12]. For PCI measurement, a programmed hydrogen amount is introduced into (or extracted from) the system using the mass flow controller. Then, the pressure increases/decreases in a value of the order of 30 kPa (5 sccm of hydrogen). To determine if the system reaches the equilibrium condition, two different criteria were used. One of them is to verify if the temporal variation of the pressure is lower than a fixed value (1.10^{-2}). The second one is to wait a selected time (1200 s). When one of these criteria is reached, it is considered that the system is in equilibrium and a point in the PCI curve is saved. Then, the software starts the following equilibrium point using again the mass flow controller.

Absorption and desorption pressure composition isotherms for the 2Mg–Co and 2MgH₂–Co mixtures were obtained in the range of 250–400 °C and up to 5.0 MPa of hydrogen pressure. The equilibrium plateau pressures were calculated as an average of the experimental points in the plateau region. Van't Hoff diagrams were plotted from the deduced equilibrium pressures. Enthalpy and entropy of formation and decomposition of each hydride were calculated from data fitting [13].

To identify the phases present at different points of PCI curves, each measurement was stopped at the desired absorbed hydrogen amount and the sample was immediately quenched to room temperature under hydrogen pressure by using cold water. After this procedure, the sample was analyzed by X-ray powder diffraction (XRPD) on a Philips PW 1710/01 instrument with Cu K α radiation using a graphite monochromator.

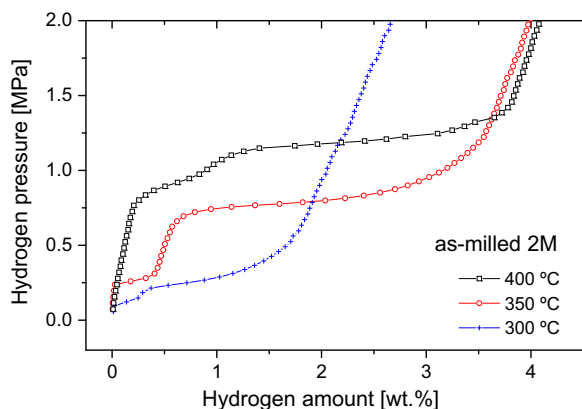


Fig. 1. Absorption PCI curves of the as-milled 2M sample without activation at different temperatures.

3. Results and discussion

3.1. Effect of hydrogen cycling on the PCIs

The study of the thermodynamic properties of the Mg–Co–H system was first performed using the 2Mg–Co mixture milled 200 h under argon (2M). To evaluate the effect of the hydrogen cycling on the shape and the hydrogen storage capacity of the PCIs, a different sample was used for each temperature. Fig. 1 shows the absorption PCI isotherms of the 2M sample at different temperatures, without previous stabilization process. From the figure, it can be observed that the total hydrogen storage capacity increases with temperature. In addition, two plateaus are identified at 300, 350 and 400 °C, being the first plateau (low pressure plateau) smaller than the second one (high pressure plateau). Moreover, independently of the temperature, the material continues absorbing hydrogen as the pressure increases. This result evidences that the 2M sample needs to be activated to favor the interaction between Mg and Co by solid state diffusion. Similar behavior was observed for AB₅ alloys [14].

We have previously demonstrated the relevance of hydrogen cycling of the 2Mg–Co mixture on the stabilization of the system, which influences the final phases obtained as well as the kinetics of the hydriding/dehydriding [10,11]. To determine the effect of hydrogen cycling on the equilibrium pressures, the 2M sample was cycled under hydrogen (about ten cycles) at 400 °C [11] and then the isotherms (absorption followed by desorption) were acquired starting from 400 °C to 250 °C, using the same as-cycled 2M sample. Fig. 2A and B displays the absorption and desorption PCIs, respectively, for the 2M sample after hydrogen cycling. From Fig. 2A, it is clearly identified at 400 °C the presence of two plateaus. The first one at about 0.75 MPa (plateau at low pressure) is flat and the other one is sloped in the hydrogen pressures range between 1.5 and 2.6 MPa (plateau at high pressure). On the other hand, at 250 °C two plateaus are hardly separated, while at 300 and 350 °C three plateaus can be ascertained. This result, i.e. the presence of three plateaus during absorption PCI curves, was not previously observed. The plateau at intermediate hydrogen pressure is referred to as intermediate plateau.

In the case of the desorption PCIs (Fig. 2B), at all temperatures we can recognize two flat plateaus, which are clearly differentiated at 400 °C and hardly at temperature lower than 350 °C. Table 2 summarizes the absorption and desorption equilibrium plateau pressures as a function of temperature and the hydrogen storage capacity associated to each plateau. Furthermore, it can be seen that the equilibrium hydrogen pressures for absorption and desorption differ specifically for the upper plateau (related with

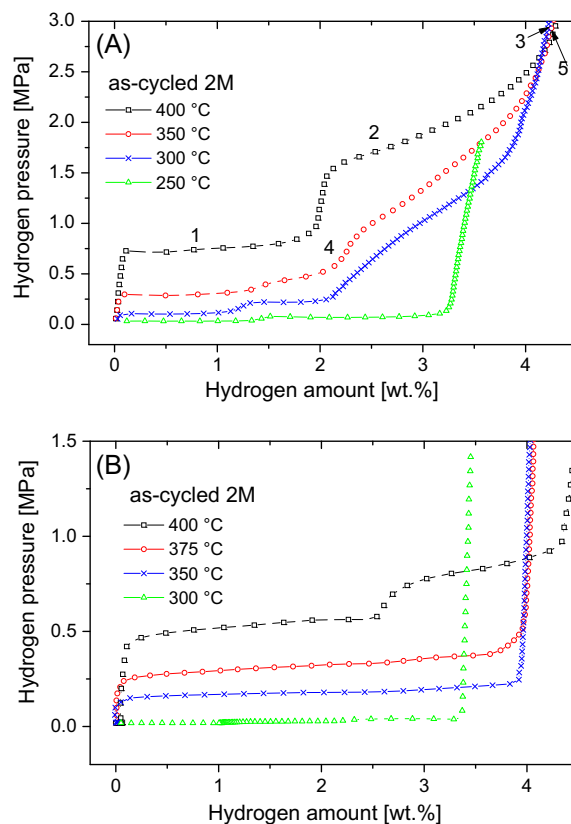


Fig. 2. PCI curves of the as-cycled 2M sample at different temperatures (after ten hydrogen cycles). (A) Absorption. (B) Desorption.

the Mg₂CoH₅ formation/decomposition). This phenomenon is known as hysteresis and it was previously reported as important for Mg₂CoH₅ [7]. The hysteresis decreased with increasing temperature due to the smaller free energy loss at higher temperature. Hysteresis contains contributions from plastic deformation, hydrogen dissociation and hydride nucleation processes [15].

To clarify the nature of the hydride phases formed during hydrogen absorption at different hydrogen pressure, XRPD analyses were performed. Fig. 3A summarizes XRPD patterns of the samples extracted at each point indicated of the isotherm at 400 °C (Fig. 2A). During the plateau at low pressure (point 1), the only hydride formed is Mg₆Co₂H₁₁, while at the end of the high pressure plateau both Mg₆Co₂H₁₁ and Mg₂CoH₅ are detected, with the first phase as the majority phase. However, the sample taken out in the point 3 evidenced the presence of both complex hydrides and the relative amount of Mg₂CoH₅ has grown. The relative fraction of Mg₂CoH₅ increases with hydrogen pressure during high pressure plateau, confirming that this plateau is associated with the Mg₂CoH₅ formation. Similar conclusion was obtained for the phases formed at 300 y 350 °C from the diffraction patterns obtained at the end of the corresponding PCIs. Fig. 3B shows the XRPD patterns of the samples stopped at points 4 and 5 of the isotherm at 350 °C (Fig. 2A). At the end of the intermediate plateau it is clear the presence of Mg and Co phases as well as the presence of Mg₆Co₂H₁₁ and MgH₂ hydrides. The detection of minor amounts of Mg₂CoH₅ cannot be discarded. At the end of the isotherm at 350 °C (high pressure plateau completed), the main phases are Mg₆Co₂H₁₁ and Mg₂CoH₅, with a major relative amount of Mg₂CoH₅. Then, in similar way than 400 °C, the low pressure plateau is associated with the formation of Mg₆Co₂H₁₁ and the high pressure plateau (the last one for the sample with three plateaus) is associated with the formation of Mg₂CoH₅, which coexist with Mg₆Co₂H₁₁. The intermediate plateau is characterized with the formation of MgH₂.

Table 2

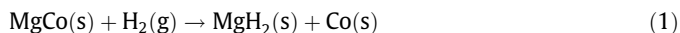
Equilibrium pressures and relative amount of hydrogen stored in the 2M and 2MH samples obtained from the absorption/desorption PCI curves.

Temperature (°C)	Plateau pressure	Hydride	Equilibrium pressure (kPa)	Hydrogen stored (wt%)
<i>Absorption for as-cycled 2M</i>				
400	Low	Mg ₆ Co ₂ H ₁₁	755	1.9
	High	Mg ₂ CoH ₅	1930 ^a (1525–2540)	2.0
350	Low	Mg ₆ Co ₂ H ₁₁	298	1.3
	Intermediate	–	467	0.7
	High	Mg ₂ CoH ₅	(820–2540) ^b	1.7
300	Low	Mg ₆ Co ₂ H ₁₁	113	1.1
	Intermediate	–	237	0.7
	High	Mg ₂ CoH ₅	(510–2530) ^b	1.8
250	Low	Mg ₆ Co ₂ H ₁₁	30	1.3
	High	Mg ₂ CoH ₅	70	1.7
<i>Desorption for as-cycled 2M</i>				
400	High	Mg ₂ CoH ₅	820	1.6
	Low	Mg ₆ Co ₂ H ₁₁	525	2.4
375	High	Mg ₂ CoH ₅	380	1.5
	Low	Mg ₆ Co ₂ H ₁₁	311	2.4
350	High	Mg ₂ CoH ₅	219	1.5
	Low	Mg ₆ Co ₂ H ₁₁	172	2.4
325	High/low	Mg ₂ CoH ₅ /Mg ₆ Co ₂ H ₁₁	97	3.6
	High/low	Mg ₂ CoH ₅ /Mg ₆ Co ₂ H ₁₁	54	3.3
<i>Desorption for 2MH</i>				
425	Unique	Mg ₂ CoH ₅	845	3.9
400	Unique	Mg ₂ CoH ₅	479	4.0
375	Unique	Mg ₂ CoH ₅	262	4.0
350	Unique	Mg ₂ CoH ₅	139	3.9
325	Unique	Mg ₂ CoH ₅	77	4.0

^a Selected equilibrium pressure determined in the pressure range specified.

^b Selected equilibrium pressure determined from uncycled sample.

The influence of hydrogen cycling on the PCI shape is clearly showed in Fig. 4. In fact, at 350 °C the 2M sample displays two or three plateaus depending of it was uncycled or cycled, respectively. The intermediate plateau appears as a consequence of cycling. In addition, the high pressure plateau in the as-cycled sample is different to the second one in the uncycled sample, involving a wide range of hydrogen pressures. The changes observed suggest the formation of a new phase in the intermediate plateau that influences the equilibrium hydrogen pressure of the high pressure plateau. Considering that the hydrogen absorption at 350 °C is performed after the desorption isotherm at 375 °C, we conclude that the formation of MgCo intermetallic compound has occurred during the previous desorption. Our previous work reveals that MgCo formation is possible after dehydrogenating up to 400 °C of as-milled 2M and also at lower temperature if the 2Mg–Co mixture was previously cycled [11]. In fact, we have demonstrated that MgCo is an intermediate compound in the formation of Mg₂CoH₅ during cycling. Then, MgCo is present in the sample after desorption at 400 °C and 375 °C, together with free Mg and Co. As confirmation, MgCo intermetallic compound is detected in the middle of the first plateau at 400 °C (curve 1 Fig. 3A). Therefore, as absorption PCI at 350 °C is performed after desorption PCI at 375 °C, the sample consists of Mg, Co and MgCo intermetallic. In this case, an intermediate plateau is clearly identified. On the basis of previous studies [11] and the XRPD showed in Fig. 3B (curve 4), this intermediate plateau could be associated with the following disproportionation reaction:



The above results provide evidence about the formation of MgH₂ from MgCo and hydrogen (reaction (1)). This reaction cannot arise during the first absorption cycle due to the absence of MgCo.

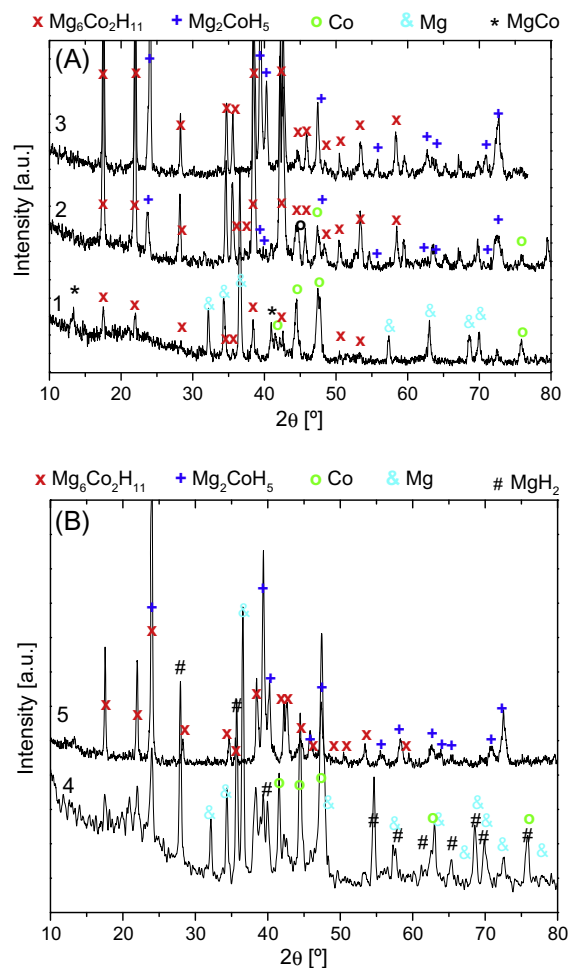


Fig. 3. XRPD patterns of 2M sample extracted at different stages indicated in Fig. 2(A). (A) 400 °C. (B) 350 °C.

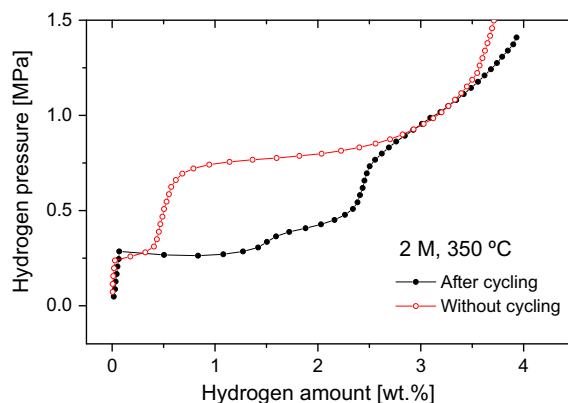


Fig. 4. Effect of the hydrogen cycling on absorption PCI curve at 350 °C.

Then, the intermediate plateau is only observed at those temperatures where the MgCo formation occurred during the previous desorption PCI curves at enough temperature (350–400 °C) and during long periods (12 h each isotherm) to favor solid state diffusion of Mg and Co. In the PCI curve at 400 °C, this intermediate plateau might be superposed with the low pressure plateau.

As a reference material and to compare with the previous thermodynamic measurements of the 2M sample, PCIs were evaluated for 2MH sample. To ensure no structural changes in the starting

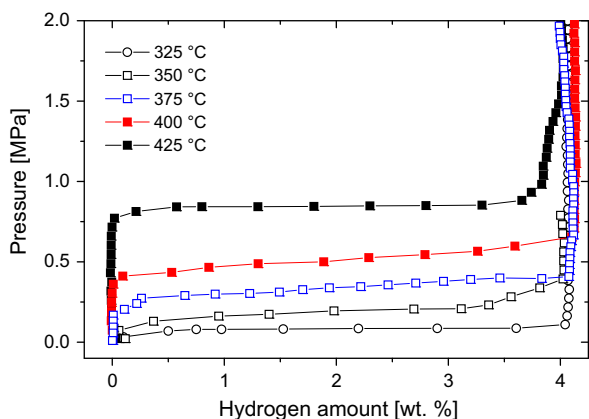


Fig. 5. Desorption PCI curves of 2MH sample (mainly Mg_2CoH_5) at different temperatures.

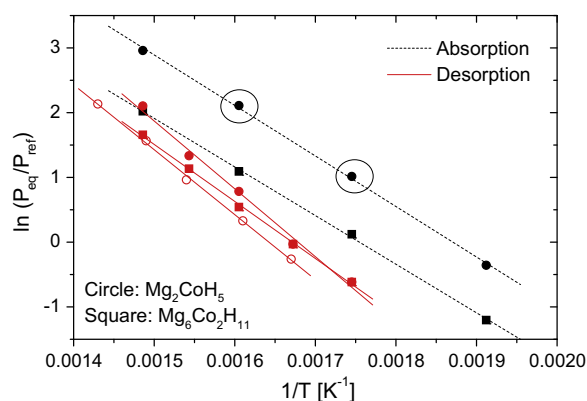


Fig. 6. Absorption and desorption van't Hoff plots of the 2M and 2MH samples. P_{ref} is the thermodynamic reference pressure ($P_{\text{ref}} = 101.3 \text{ kPa}$). Solid symbol: 2M; hollow symbol: 2MH. Circle: Mg_2CoH_5 ; square: $\text{Mg}_6\text{Co}_2\text{H}_{11}$.

material, which consists mainly of Mg_2CoH_5 [10], a different sample was used for each desorption isotherm. The 2MH sample was heated under 5.0 MPa of hydrogen pressure from room temperature up to the selected temperature. Fig. 5 shows the representative PCI curves. There exists only one plateau region corresponding to desorption of Mg_2CoH_5 . The estimated equilibrium pressures are indicated in Table 2. From the plateau length, the phase abundance of Mg_2CoH_5 can be estimated which agrees with the previously reported yield (>80%) [10].

3.2. Thermodynamic evaluation: Van't Hoff diagram

The equilibrium properties of the different Mg–Co–H hydrides obtained from 2M and 2MH samples were examined between 425 and 250 °C. The thermodynamic parameters (absorption/desorption enthalpies and entropies) of these complex hydrides were calculated from the van't Hoff graphs. In Fig. 6 the plots of $\ln P(\text{equilibrium})/P(\text{reference})$ versus T^{-1} for the formation/decomposition of $\text{Mg}_6\text{Co}_2\text{H}_{11}$ and Mg_2CoH_5 are shown, based on data listed in Table 2. The graphs can be fitted by a straight line with its slope being a measure of enthalpy (ΔH) and the intercept a measure of entropy (ΔS). In all cases the equilibrium hydrogen pressure for $\text{Mg}_6\text{Co}_2\text{H}_{11}$ (first plateau during absorption and second plateau during desorption) was determined unequivocally. For the 2M sample after cycling and in those temperatures where three plateaus were observed, the equilibrium pressure for Mg_2CoH_5 (high pressure plateau during absorption and desorption)

Table 3

Formation and decomposition enthalpies and entropies obtained from the van't Hoff plot for 2M and 2MH samples.

Sample	Hydride	ΔH (kJ/mol)		ΔS (J/K mol)	
		Absorption	Desorption	Absorption	Desorption
2M	Mg_2CoH_5	-65 ± 2	-86 ± 3	121 ± 2	126 ± 1
	$\text{Mg}_6\text{Co}_2\text{H}_{11}$	-62 ± 2	-75 ± 1	110 ± 2	137 ± 1
2MH	Mg_2CoH_5	–	-84 ± 2	–	137 ± 1

was determined from the un-cycled 2M sample (Fig. 1). The reason of this criterion is to avoid the influence of the additional plateau observed at intermediate pressures during absorption.

In Table 3 the values of enthalpy and entropy for each hydride phase are shown, and they can be compared with previous works (Table 1). The assessed hydrides possess thermodynamics parameters that are in the range of the values reported in the literature. However, there are details that are interesting to remark. Only one previous work, which is from our group, accounts for the enthalpy formation value for $\text{Mg}_6\text{Co}_2\text{H}_{11}$, being of $\Delta H = -63 \text{ kJ/mol H}_2$ [9]. The value calculated in the present work is the same, i.e. $\Delta H = -62 \text{ kJ/mol}$. Moreover, four previous works report the decomposition enthalpy value of $\text{Mg}_6\text{Co}_2\text{H}_{11}$, that range between $\Delta H = -65$ to $\Delta H = -95 \text{ kJ/mol}$ [3,5,6,8,9]. In the present work, the decomposition enthalpy value derived from the shorter plateau of $\text{Mg}_6\text{Co}_2\text{H}_{11}$ is $\Delta H = -73 \text{ kJ/mol}$, which is practically the equal that three previous works [3,6,8]. These results evidence that the hydrogen pressure determined for the formation and decomposition of $\text{Mg}_6\text{Co}_2\text{H}_{11}$ are not strongly modified as a consequence of cycling. It is important to highlight that no thermodynamic studies in the literature were performed using pure $\text{Mg}_6\text{Co}_2\text{H}_{11}$.

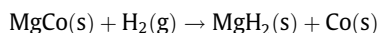
In the case of Mg_2CoH_5 , the cycling of the 2M sample modifies notably the shape of the last plateau during absorption. In fact, this plateau is strongly sloped and it extends in a wide range of hydrogen pressure. Reiser et al. [6] commented the difficulty to estimate formation enthalpy value after hydrogen cycling for the Mg_2CoH_5 . For these reasons, for those temperatures where the PCIs display three plateaus, the equilibrium pressures were determined using un-cycled sample. The enthalpy values corresponding to formation/decomposition of Mg_2CoH_5 are $\Delta H = -65$ y $\Delta H = -82 \text{ kJ/mol}$, respectively. These values are in good agreement with previous values obtained by [1,7,8]. Clearly, the cycling favors the formation of MgCo intermetallic during decomposition and modifies the thermodynamic system under study.

In particular, it is interesting to determine the enthalpy decomposition value obtained from 2MH consisting mainly in Mg_2CoH_5 . For this sample, only one plateau during hydrogen desorption is detected and the pressure could be determined without doubt. The decomposition ΔH value obtained for the 2MH sample, which consist majority of Mg_2CoH_5 , is the same considering the experimental error, that the calculated for 2M (using equilibrium pressure values from cycled and uncycled samples). Furthermore, the Mg–Co–H hydrides display values of ΔH in the same order of magnitude than that reported for MgH_2 . Then, the hydrides $\text{Mg}_6\text{Co}_2\text{H}_{11}$, Mg_2CoH_5 and MgH_2 have very close stability.

4. Conclusions

The 2Mg–Co mixture was prepared by mechanical milling under argon to allow a homogeneous Co dispersion in the Mg matrix and a refinement of the microstructure of both Mg and Co metals (2M sample). In addition, the 2MgH₂–Co mixture was used to synthesize Mg_2CoH_5 by reactive mechanical alloying under hydrogen (2MH sample). Both starting materials were used to analyze the thermodynamic behavior during hydrogen cycling. The main conclusions for the Mg–Co–H are as follows:

- (1) The absorption PCI curves at different temperatures for cycled 2M show two or three plateaus. XRPD information allows correlating the plateau at low hydrogen pressure with the formation of $\text{Mg}_6\text{Co}_2\text{H}_{11}$, while the second or third plateau (high pressure plateau) with the formation of Mg_2CoH_5 .
- (2) For the cycled 2M, the presence of an intermediate plateau associated with the MgCo formation is observed at 300 and 350 °C. The hydride formation which occurs during this intermediate plateau can be represented as:



The intermetallic MgCo is formed during previous dehydriding step from the mixture $\text{Mg}_6\text{Co}_2\text{H}_{11}$ – Mg_2CoH_5 .

- (3) The formation and decomposition enthalpy of $\text{Mg}_6\text{Co}_2\text{H}_{11}$ are $\Delta H = -62$ kJ/mol and $\Delta H = -75$ kJ/mol, respectively. A comparison with previous reported data proves that the hydrogen equilibrium pressure of $\text{Mg}_6\text{Co}_2\text{H}_{11}$ is practically unaffected by cycling. On the contrary, no consistent value for the formation enthalpy for Mg_2CoH_5 could be calculated using hydrogen pressure after cycling.
- (4) Decomposition enthalpy value for Mg_2CoH_5 estimated from 2MH sample ($\Delta H = -84$ kJ/mol) is equal to that calculated from the equilibrium pressure for un-cycled 2M ($\Delta H = -86$ kJ/mol). In addition, these values are in the order of magnitude of those reported in the literature.
- (5) The three hydrides formed in the Mg–Co–H system, i.e. $\text{Mg}_6\text{Co}_2\text{H}_{11}$, Mg_2CoH_5 and MgH_2 , show similar thermodynamic stability.

Acknowledgments

This study has been partially supported by CONICET (National Council of Scientific and Technological Research), CNEA (National

Commission of Atomic Energy), ANPCyT (PICT N° 1049) and Instituto Balseiro (University of Cuyo).

References

- [1] P. Zolliker, K. Yvon, P. Fisher, J. Schefer, Dimagnesium cobalt(1) pentahydride, Mg_2CoH_5 , containing square-pyramidal pentahydrocobaltate(4-) (CoH_5 4-) anions, *J. Inorg. Chem.* 24 (1985) 4177–4180.
- [2] I.G. Konstanchuk, E.I. Ivanov, A.A. Stepanov, T.I. Samsonova, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk* 3 (1989) 93–98 (in Russian).
- [3] E.J. Ivanov, I.G. Konstanchuk, A. Stepanov, Y. Jie, M. Pezat, B. Darriet, The ternary system magnesium–cobalt–hydrogen, *Inorg. Chem.* 28 (1989) 613–615.
- [4] J.F. Stampfer Jr., C.E. Holley Jr., J.F. Suttle, *J. Am. Chem. Soc.* 82 (1960) 3504–3508.
- [5] M. Yoshida, F. Bonhomme, K. Ivon, On the composition and structure of the cubic g-phase in the Mg–Co–H system, *J. Alloys Comp.* 190 (1993) L45–L46.
- [6] A. Reiser, B. Bogdanovick, K. Schlichte, The application of Mg-based metal-hydrides as heat energy storage systems, *Int. J. Hydrogen Energy* 25 (2000) 425–430.
- [7] J. Chen, H.T. Takeshita, D. Chartouni, N. Kuriyama, T. Sakai, Synthesis and characterization of nanocrystalline Mg_2CoH_5 obtained by mechanical alloying, *J. Mater. Sci.* 36 (2001) 5829–5834.
- [8] H. Shao, H. Xu, Y. Wang, X. Li, Synthesis and hydrogen storage behavior of Mg–Co–H system at nanometer scale, *J. Solid State Chem.* 177 (2004) 3626–3632.
- [9] I. González, F.C. Gennari, G.O. Meyer, Influence of sintering parameters on formation of Mg–Co hydrides based on their thermodynamic characterization, *J. Alloys Comp.* 462 (2008) 119–124.
- [10] M.G. Verón, A. Condó, F.C. Gennari, Effective synthesis of Mg_2CoH_5 by reactive mechanical milling and its hydrogen sorption behavior after cycling, *Int. J. Hydrogen Energy* 38 (2013) 973–981.
- [11] M.G. Verón, F.C. Gennari, G.O. Meyer, Role of Mg–Co compound on the sorption properties of the Mg–Co milled mixtures, *J. Power Sources* 195 (2) (2010) 546–552.
- [12] G. Meyer, D.S. Rodríguez, F. Castro, G. Fernández, Hydrogen Energy Progress, in: Proceedings of the 11th World Energy Conference, Stuttgart, Germany, 1293, 23–29 Junio, 1996.
- [13] G. Sandrock, A panoramic overview of hydrogen storage alloys from a gas reaction point of view, *J. Alloys Comp.* 293–295 (1999) 877–888.
- [14] G. Liang, J. Huot, R. Schulz, Hydrogen storage properties of the mechanically alloyed LaNi_5 -based materials, *J. Alloys Comp.* 320 (2001) 133–139.
- [15] P.S. Rudman, G. Sandrock, Metallurgy of rechargeable hydrides, *Annu. Rev. Mater. Sci.* 12 (1982) 271–294.