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Journal of Alloys and Compounds 356–357 (2003) 588–592
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Synthesis of hydrides by mechanical alloying in the Mg–Ni–Ge system

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Received 4 July 2002; accepted 3 October 2002

Abstract

We investigated the mechanical alloying (MA) of 2Mg–0.5Ni–0.5Ge mixture at room temperature under hydrogen atmosphere. The evolution of the phases during MA process and the thermal stability of the obtained hydrides were studied using XRD, DSC, DTA and TG. Formation of MgH_2 and Mg_2NiH_4 was observed at short milling times. Unreacted Ge in the product reduces the desorption temperature of MgH_2 in more than 100 °C. As the milling time increases, the MA leads to the formation of a new Mg-based hydride in the Mg–Ni–Ge system. This novel hydride has a hydrogen content higher than 1 wt.% and is stable upon heating up to 410 °C. We present an alternative synthesis route for the Mg–Ni–Ge hydride that involves the MA of the 2Mg–0.5Ni–0.5Ge mixture under argon followed by short milling times under hydrogen atmosphere. Our results show that the ternary alloy obtained by milling of the 2Mg–0.5Ni–0.5Ge mixture under argon, with Mg_3MNi_2-type cubic structure, is the precursor of the novel Mg–Ni–Ge hydride.

Keywords: Hydrogen storage material; Mechanical alloying; X-ray diffraction; Thermal analysis; Calorimetry

1. Introduction

Hydrides based on intermetallic compounds have been found to be excellent hydrogen storage materials. This is the case of Mg_2Ni [1,2] which reacts readily with gaseous hydrogen forming the solid solution $Mg_2NiH_{0.3}$ and, after further hydrogen absorption at high temperature, the cubic hydride phase Mg_2NiH_4.

In recent years, much effort has been devoted to improve the performance of Mg–Ni alloys. In particular, the use of the mechanical alloying (MA) technique [3,4] and/or partial substitution of Mg or Ni by a third element (M) to form ternary phases such as $Mg_2Ni_{1-x}M_x$ [5,6] or $Mg_{2-x}M_xNi$ [7,8] have been investigated. MA has emerged as a very interesting technique to obtain alloys [9,10] or hydrides [11,12], since the structural and microstructural modifications introduced during milling favor hydrogen absorption/desorption kinetics. It was also observed that the appropriate addition of a third metal improves the hydrogen absorption/desorption kinetics with respect to Mg_2Ni. These ternary alloys [5,6] usually preserve the hexagonal structure of Mg_2Ni, with partial substitution of Ni or Mg by M. Among the few exceptions to that rule are the cases of the cubic phase of the type Mg_3MNi_2 in $Mg_{2-x}M_xNi$ with M=Al, Ti prepared at high pressure/temperature conditions [8] or the recently reported synthesis of a new alloy in the Mg–Ni–Ge system obtained by MA [13].

Previous reports showed evidence of strong and localized hydrogen–metal bonds in hydrides obtained from Mg_2Ni or $Mg_2Ni_{1-x}M_x$. Based on the study of the configuration of the NiH_4 complex in Mg_2NiH_4 by total-energy calculations [14], it was demonstrated that the charge distribution in cubic Mg_2NiH_4 strongly resembles that of the family of Mg_2X compounds (X=Si, Ge, Sn, Pb, FeH_6 and CoH_5), confirming that the $(NiH_4)^{4-}$ entity is similar to the IVB^{4-} ions. Thus, Mg_2NiH_4 can be considered a member of the Mg_2X family of compounds with antifluorite structure. In this family, a regularity in the lattice parameters, charge distributions, and the ionic bonding between the $(IVB)^{4-}$ cluster and the Mg^{2+} ions was observed [14]. In particular, it was shown the strong equivalence between the tetravalent entities Ge^{4-} and $(NiH_4)^{4-}$.

In this work, we produced Mg–Ni–M alloys by reactive mechanical alloying (RMA) with Ge as the third metal and hydrogen atmosphere as gaseous reacting agent. We select

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0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00144-0

a starting global composition of 2Mg–0.5Ni–0.5Ge to achieve partial substitution of Ni by Ge in the $(NiH_4)^{4-}$ cluster. We analyze the effect of milling time under hydrogen atmosphere on the synthesis of hydrides and their thermal stability. We successfully synthesize a novel ternary hydride in the Mg–Ni–Ge system via MA under hydrogen atmosphere at room temperature. We also provide an alternative procedure for the production of this new ternary hydride.

2. Experimental

Elemental powdered magnesium, germanium and nickel (purity 99.9%) were used. The powders in global composition 2Mg–0.5Ni–0.5Ge were mechanically milled under argon (99.995%, AGA, Argentina) and hydrogen (99.995%, Air Liquid, Argentina) using a Uni-Ball-Mill II apparatus (Australian Scientific Instruments). The mixture together with ferromagnetic steel balls were put into a stainless steel container and closed in an argon glove box. In all experiments, about 6 g of starting materials were used, resulting in a ball to powder weight ratio of 44:1. The pressure inside the container was 0.1 or 0.5 MPa when milling under argon or hydrogen atmosphere, respectively. In RMA experiments the container was systematically refilled every 20 h to guarantee Mg hydrogenation.

At regular time intervals, the container was opened inside an argon glove box and a small amount of powder was taken for analysis by X-ray powder diffraction (XRD), differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) techniques. X-ray powder diffraction was performed on a Philips PW 1710/01 instrument with Cu Kα radiation. The thermal behavior of the hydrides was studied by DSC (DSC 2910, TA Instruments) using heating rates of 6, 10 and 25 °C min^{-1}, with an argon flow rate of 18 ml min^{-1}. In addition, DTA-TG (Netzch STA 409) measurements were carried out under argon atmosphere using a heating rate of 6 °C min^{-1} and an argon flow rate of 50 ml min^{-1}. The hydrogen content of selected samples was measured using a LECO H_2 analyzer, where the sample is melted and the amount of hydrogen released is measured by the change of the thermal conductivity of the carrier due to the hydrogen gas.

3. Results and discussion

3.1. Synthesis of hydrides by RMA of the 2Mg–0.5Ni–0.5Ge mixture

Fig. 1 shows the evolution of X-ray diffraction patterns as a function of milling time for the 2Mg–0.5Ni–0.5Ge mixture during RMA. For comparison, we also show the X-ray diffraction pattern of the starting mixture. We observe the formation of Mg_2Ge and tetragonal MgH_2 after 20 h. The intensity of the Mg_2Ge peaks grows with milling time, while that corresponding to the MgH_2 decrease, disappearing after 60 h. The hydride Mg_2NiH_4 (probably a mixture of low and high temperature phases [9]) begins forming at about 40 h. As milling time increases the intensity of the peaks corresponding to Ge and Ni decreases, and they are hardly detected after 60 h. Two main changes were observed. First, the apparition of an important set of unidentified diffraction peaks, which we associate with the formation of a novel hydride in the Mg–Ni–Ge system. Second, the detection of an amorphous phase. Further milling enhances atom reordering and crystallization of Mg–Ni–Ge hydride. After 90 h of RMA we clearly identify two phases: Mg_2Ge and the Mg–Ni–Ge hydride. We do not observe any change in the formed phases if RMA is continued up to 200 h, only an increase in the intensity of the peaks and higher crystallinity of the new hydride. Although we suspect the presence of MgO in the sample after prolonged milling, as reported in previous works [11,15], we cannot distinguish it unequivocally.

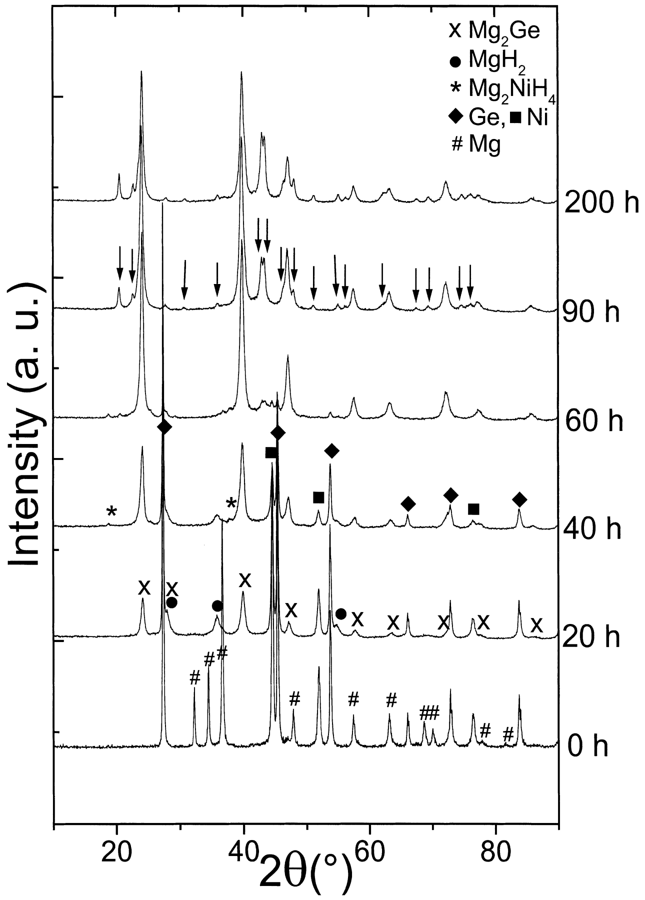

Fig. 1. XRD patterns of the 2Mg–0.5Ni–0.5Ge mixture after RMA as a function of milling time. Arrows indicate the new Mg–Ni–Ge hydride peaks.

Our previous studies on MA of Mg–Ni–Ge mixtures under argon [13] are useful to understand the reactivity of this system after RMA under hydrogen (Fig. 2a). When we milled a 2Mg–0.5Ni–0.5Ge mixture under argon, we observed the formation of a new ternary alloy with Mg_3MNi_2-type cubic structure and lattice parameter $a=$ 11.52 Å, simultaneously with the formation of Mg_2Ge. This new alloy was produced after 90 h and it persisted after further milling up to 200 h. This result suggests that the Mg–Ni–Ge alloy produced by MA under argon is the precursor of the novel hydride formed after RMA of a 2Mg–0.5Ni–0.5Ge mixture, being in both cases Mg_2Ge the only additional phase. Considering this possibility, we perform MA of a 2Mg–0.5Ni–0.5Ge mixture under argon until complete formation of the Mg_3MNi_2-type alloy (M= Ge) was observed. Fig. 2a shows XRD patterns of the mixture Mg_2Ge and Mg_3MNi_2-type alloy produced after MA under argon [13]. Then, we changed the gaseous atmosphere to hydrogen to favor the formation of the novel Mg–Ni–Ge hydride. Fig. 2b and c show XRD patterns of the as-milled sample (Fig. 2a) after 20 and 40 h of milling under hydrogen, respectively. We identify the formation of the novel hydride in the Mg–Ni–Ge system after 20 h of RMA. Some diffraction peaks corresponding to the Mg_3MNi_2-type alloy are also detected. After 40 h we observe the coexistence of Mg–Ni–Ge hydride and Mg_2Ge. This indicates that MA of a 2Mg–0.5Ni–0.5Ge mixture under argon followed by RMA under hydrogen during few hours provides an alternative route to the formation of Mg–Ni–Ge hydride. Additional milling under argon (Fig. 2d) produces slight changes in the XRD pattern of the novel hydride, for example some diffraction peaks become sharper, allowing us to conclude that this Mg–Ni–Ge hydride remains stable during MA under argon.

3.2. Desorption behavior of the hydrides formed by RMA of the 2Mg–0.5Ni–0.5Ge mixture

DSC measurements of hydrides produced by RMA of the 2Mg–0.5Ni–0.5Ge mixture were performed to analyze their thermal stability, Fig. 3. Table 1 summarizes the

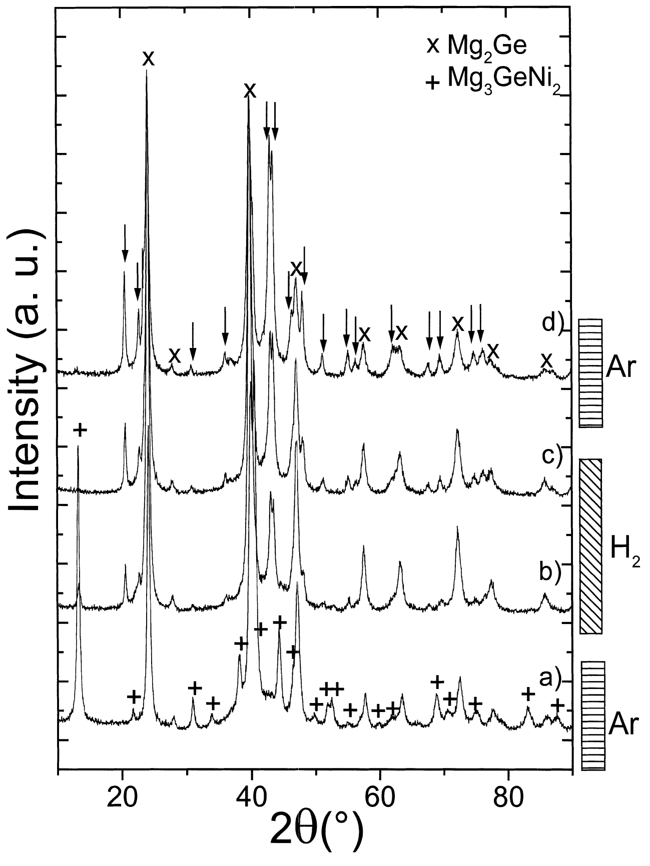

Fig. 2. XRD pattern of the 2Mg–0.5Ni–0.5Ge mixture after: (a) MA for 200 h under argon; (b) same as (a) plus 20 h of MA under hydrogen; (c) same as (a) plus 40 h of MA under hydrogen; and (d) same as (c) plus 40 h of MA under argon. Arrows indicate the new Mg–Ni–Ge hydride peaks.

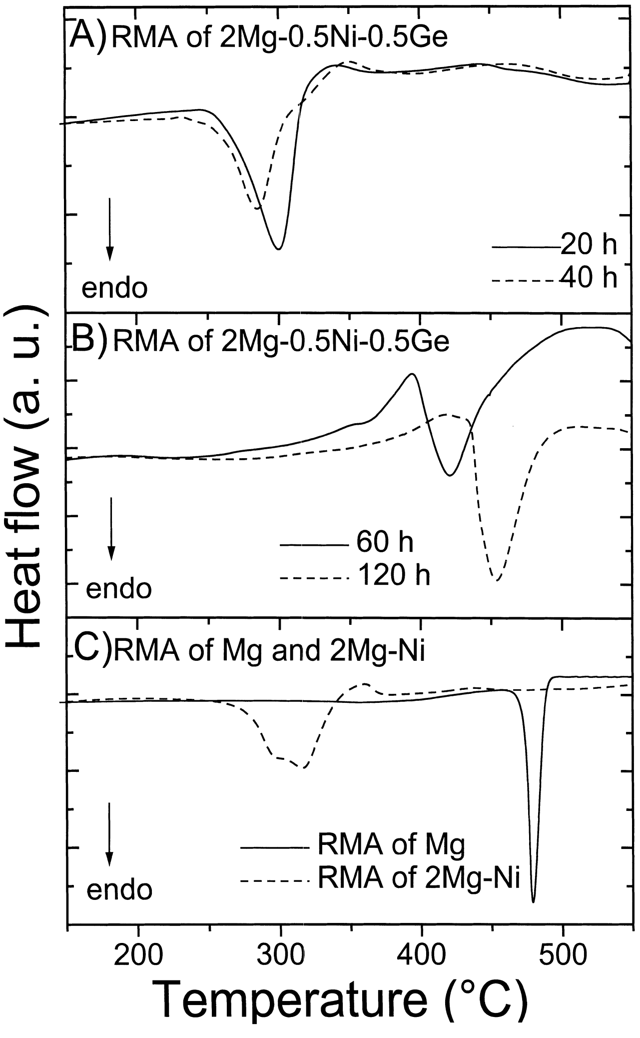

Fig. 3. (A) DSC curves of the 2Mg–0.5Ni–0.5Ge mixture after RMA for 20 and 40 h (25 °C min^{-1}); (B) DSC curves of the 2Mg–0.5Ni–0.5Ge mixture after RMA for 60 and 120 h (10 °C min^{-1}); and (C) DSC curves for Mg and 2Mg–Ni after RMA for 20 and 270 h, respectively (25 °C min^{-1}).

Table 1
Phases detected by XRD and characteristic thermal desorption temperatures of the hydrides as a function of milling time

Milling time (h)	Phases detected by XRD	DSC	
		T_{onset} (°C)	T_{peak} (°C)
20	MgH_2, Mg_2Ge, Mg, Ni, Ge	243	300
40	MgH_2, Mg_2NiH_4, Mg_2Ge, Ni, Ge	233	285
60	Mg–Ni–Ge hydride, Mg_2NiH_4, Mg_2Ge, Ni, Ge	395	421
120	Mg–Ni–Ge hydride, Mg_2Ge	420	453
200	Mg–Ni–Ge hydride, Mg_2Ge	431	467

hydrides obtained after RMA (Fig. 1) and the values of the onset and peak temperatures (T_{onset} and T_{peak}, respectively) of the endothermic peaks of Fig. 3 as a function of milling time. XRD analyses performed on the samples after DSC runs confirm the complete decomposition of the hydrides during heating.

Two distinct behaviors associated to the presence of different hydrides as a function of milling time are identified in Fig. 3. For milling times up to 40 h, Fig. 3A shows the DSC signal corresponding to MgH_2 and MgH_2–Mg_2NiH_4 mixture obtained after 20 and 40 h of RMA, respectively (Table 1). We identify sharp endothermic peaks at temperatures lower than 300 °C. For higher milling times Fig. 3B shows the DSC signal from hydrogen desorption of the Mg_2NiH_4–new hydride mixture or only the Mg–Ni–Ge hydride, observed at temperatures higher than 390 °C. For comparison, Fig. 3C shows the DSC measurement of MgH_2 samples produced by RMA of Mg after 20 h [11] and Mg_2NiH_4 formed after RMA of a 2Mg–Ni mixture after 270 h.

To analyze the influence of Ge and Ni on hydrogen desorption temperature of MgH_2 and Mg_2NiH_4, we compare Fig. 3A and C. When MgH_2 is synthesized by RMA of Mg, i.e. without Ge and Ni, we observe that MgH_2 obtained after 20 h of milling decompose at 463 °C (Fig. 3C). Surprisingly, when the 2Mg–0.5Ni–0.5Ge mixture is processed by RMA, the decomposition of MgH_2 obtained after 20 h of milling is observed at 300 °C (Fig. 3A). As the milling time of both samples is the same, the structural changes introduced during RMA are similar. Then, the strong reduction in hydrogen desorption temperature in more than 150 °C is associated to the Ge or Ge–Ni presence in the starting mixture. We have recently demonstrated that the presence of Ge is responsible for the reduction in the hydrogen desorption temperature [15]. We observed that Ge has a catalytic effect on the hydrogen desorption from MgH_2, which depends on the proportion of Ge and increases with a better intermixing and particle size reduction induced by milling [15].

In the case of hydrogen desorption from Mg_2NiH_4 we observe that the decomposition temperature for Mg_2NiH_4 produced by RMA of the 2Mg–Ni mixture (316 °C, Fig. 3C) is similar to that for the MgH_2–Mg_2NiH_4 formed by RMA of the 2Mg–0.5Ni–0.5Ge mixture (285 °C, Table 1). In both samples, we identify two exothermic peaks at 360 and 438 °C, which correspond to the crystallization of Mg_2Ni and $MgNi_2$, respectively [16]. Then, the presence of Ge does not have a clear effect on the Mg_2NiH_4 thermal stability. Moreover, we observe in Fig. 3A a reduction in the hydrogen desorption temperature of ≈15 °C of MgH_2 (20 h of milling) and MgH_2–Mg_2NiH_4 (40 h of milling) with milling time, associated to particle size reduction and microstructural modifications induced by RMA [11,12].

For milling times higher than 60 h, Fig. 3B shows an endothermic peak that shifts towards higher temperatures as milling time increases. This shift is a consequence of the increasing amount of the new hydride (Table 1). For 60 h of milling the endothermic peak can still be associated to the Mg_2NiH_4–novel hydride mixture decomposition. As milling time increases the proportion of the Mg–Ni–Ge hydride grows and the endothermic peak shifts towards higher temperatures and becomes sharper. For 120 h of milling the endothermic peak at 450 °C is associated mainly to novel hydride decomposition.

In order to characterize the thermal stability and the hydrogen content of the new Mg–Ni–Ge hydride, we perform DTA/TG and DSC studies on the 2Mg–0.5Ni–0.5Ge mixture after RMA for 200 h. Fig. 4A shows DTA and TG curves of Mg–Ni–Ge hydride formed by RMA after 200 h of milling. Fig. 4B shows the DSC curve of the same sample. From DTA (Fig. 4A) and DSC (Fig. 4B) curves, we identify a clear endothermic peak corresponding to the hydrogen desorption from the Mg–Ni–Ge hydride, with a T_{onset} of 410 and 431 °C, respectively. The temperature difference can be attributed to the fact that sample preparation and disposition were different for each technique. The heat flow associated with the process is 0.034 J g^{-1}. From XRD patterns performed on the samples after DTA and DSC runs we identify the Mg–Ni–Ge alloy, Mg_2Ge and MgO as final phases, confirming that Mg_3MNi_2-type alloy is the precursor of the new hydride phase. In addition, TG analysis shows that the total relative weight loss attributed to the novel hydride decomposition is about 1%. This result is in agreement with the hydrogen content measured using LECO H_2 analyzer (0.98 wt.%). The hydrogen content determined by TG and LECO corresponds to the Mg–Ni–Ge hydride, in spite of the fact that we simultaneously synthesize Mg_2Ge. Then, the hydrogen content in the hydride phase is higher than 1 wt.%. We are developing additional studies in order to

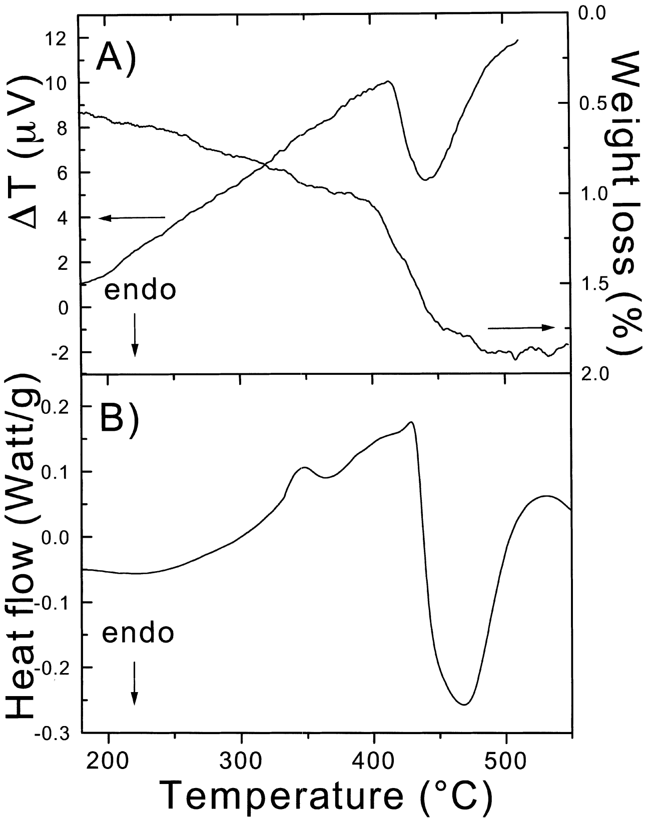

Fig. 4. Characterization of the Mg–Ni–Ge hydride synthesized by RMA of the 2Mg–0.5Ni–0.5Ge mixture for 200 h. (A) DTA and TG curves (6 °C min^{-1}) and (B) DSC curve (6 °C min^{-1}).

determine the abundance of each phase in the mixture and the crystal structure of the novel hydride.

4. Conclusions

We synthesized MgH_2, Mg_2NiH_4 and a novel hydride in the Mg–Ni–Ge system by RMA of the 2Mg–0.5Ni–0.5Ge mixture under hydrogen atmosphere. The new hydride can also be synthesized by an alternative procedure that includes MA of the 2Mg–0.5Ni–0.5Ge mixture under argon followed by RMA under hydrogen during a period of time lower than that needed if only RMA is performed. We conclude that the Mg_3MNi_2-type alloy obtained by MA under argon of the 2Mg–0.5Ni–0.5Ge mixture is the precursor of the novel Mg–Ni–Ge hydride formed by RMA.

The hydrides obtained at different milling times show two different hydrogen desorption behaviors. For milling times up to 40 h, when MgH_2 or the MgH_2–Mg_2NiH_4 mixture are formed, we observed a sharp endothermic peak at temperatures lower than 300 °C. For longer milling times, when the Mg_2NiH_4–new hydride mixture or only Mg–Ni–Ge hydride are present, we identified an endothermic peak at temperatures higher than 390 °C, which shifts towards higher temperatures as milling time increases due to the growing amount of the Mg–Ni–Ge hydride. The novel hydride decomposed when heated at 410 °C and showed a hydrogen content higher than 1 wt.%. Future work is being developed to determine the crystal structure of the novel Mg–Ni–Ge hydride and to characterize its potential use for hydrogen storage.

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