

# Thermodynamic properties and absorption–desorption kinetics of $\text{Mg}_{87}\text{Ni}_{10}\text{Al}_3$ alloy synthesised by reactive ball milling under $\text{H}_2$ atmosphere

S. Doppiu<sup>a</sup>, P. Solsona<sup>a</sup>, T. Spassov<sup>b</sup>, G. Barkhordarian<sup>c</sup>, M. Dornheim<sup>c</sup>,  
T. Klassen<sup>c</sup>, S. Suriñach<sup>a</sup>, M.D. Baró<sup>a,\*</sup>

<sup>a</sup> *Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

<sup>b</sup> *Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

<sup>c</sup> *Institute for Materials Research, GKSS Research Centre, 21502 Geesthacht, Germany*

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## Abstract

In this work, the synthesis of  $\text{Mg}_{87}\text{Ni}_{10}\text{Al}_3$  hydride by reactive ball milling under  $\text{H}_2$  atmosphere is presented. Reactive milling under hydrogen induces the conversion of Mg into nanocrystalline  $\text{MgH}_2$  (final crystallite sizes  $\sim 8$  nm). The percentage of the hydride increases with the milling time and after 20 h of mechanical treatment the reaction is complete. Only at longer milling time, when a high conversion degree of Mg into the hydride is reached, the reaction with Ni to form  $\text{Mg}_2\text{NiH}_4$  is observed. Thermal analysis shows that, for the shorter milling time, the decomposition of the hydride starts at  $\sim 200^\circ\text{C}$ , but the stability of the hydride slightly increases with increasing milling time. Fast absorption–desorption kinetics is obtained at  $300^\circ\text{C}$ .

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## 1. Introduction

It is generally known that mechanical milling is an excellent technique to produce a wide range of materials with interesting properties [1]. In mechanical treatments, carried out by ball milling, powder particles are subjected to repetitive compressive loads that promote different phenomena depending on the reacting materials. In the last years, the application of this technique to synthesise nanocrystalline materials for hydrogen storage applications has been extensively studied [2–5]. Indeed, one of the most attractive means to store hydrogen is in the form of metal hydride. Among them, Mg and Mg based alloys are considered as the most promising candidates, because of their light weight, the high amount of  $\text{H}_2$  that can be stored (7.6 wt.% for pure  $\text{MgH}_2$ ), the low cost and abundance on the earth. Nevertheless, the high decomposition

temperature and the slow hydrogen absorption–desorption kinetics are limiting factors for industrial applications. A considerable amount of work to improve the hydrogen absorption–desorption kinetics has been focused towards the preparation of nanocomposites based on  $\text{MgH}_2$  with different metal and/or metal oxide additions [6–8].

In this paper, reactive ball milling in  $\text{H}_2$  atmosphere carried out on Mg (87 at.%)Ni (10 at.%)Al (3 at.%) is presented. The microstructural evolution of the powders subjected to mechanical treatment as well as the thermal stability of the formed hydride and the absorption–desorption kinetics were studied.

## 2. Experimental

Pure elemental powders of magnesium nickel and aluminum, supplied by Aldrich, were mixed in the desired com-

\* Corresponding author. Tel.: +34 93 5811657; fax: +34 93 5812155.

E-mail address: dolors.baró@uab.es (M.D. Baró).

position and milled in a planetary mill (Fritsch Pulverisette 5) at 300 rpm under 6 bar of hydrogen pressure. Modified stainless steel vials, to allow milling under different atmosphere, were used together with 11 stainless steel balls (12 mm diameter) with a ball to powder mass ratio (BPR) 15:1. In order to study the evolution of the reaction during milling, samplings at regular intervals of time (4, 8, 12, 16 and 20 h) were performed. The microstructural evolution upon milling was studied by X-ray diffraction analysis by using a Philips 3050 diffractometer with Cu  $K_{\alpha}$  radiation. Information about the phases formed and the relative percentages, the crystallite sizes and the microstrain level were obtained from the X-ray patterns by using a full profile fitting procedure [9] based on the Rietveld method. The thermal stability of the hydride formed and the hydrogen content were studied at different stages of the milling, by differential scanning calorimetry (DSC) and thermo-gravimetry (TG) using Perkin-Elmer DSC-7, TGA-7 equipments with a heating rate of 10 °C/min. Hydrogen sorption properties were determined by using a hydrogen titration apparatus (HERA Hydrogen Storage Systems) especially designed for fast data acquisition. Hydrogen absorption and desorption were performed at 8 bar and vacuum, respectively. Kinetic measurements were carried out at 300, 250 and 230 °C.

### 3. Results and discussion

#### 3.1. Synthesis and microstructural properties

Fig. 1 shows the x-ray diffraction pattern together with the calculated profiles, obtained from the Rietveld analysis, for the samples milled 4, 8, 12 and 20 h, respectively. The errors, obtained by subtracting the experimental and the calculated data, are also reported. As can be observed, after 4 h of milling the formation of tetragonal  $\beta$ -MgH<sub>2</sub> has already started. Increasing the milling time the percentage of the hydride increases and after 16 h of mechanical treatment complete conversion was obtained. Oxidation of the sample was observed after 8 h of milling, with the appearance of a very fine MgO phase. The degree of oxidation increases with the milling time and after 20 h a percentage of about 32 wt.% of MgO was detected. We assumed that the oxidation has occurred during either the milling or the X-ray measurements (the powders with smaller grain size, longer milling time, are more contaminated). An interesting result is that in the first stage of the milling no reaction between Mg and Ni was observed. Only after 12 h of milling, when high degree of conversion of Mg into nanocrystalline MgH<sub>2</sub> was reached (~60 wt.%), did the formation of Mg<sub>2</sub>NiH<sub>4</sub> start. The diffraction profiles analysis evidences that several processes take place upon milling. In the first stage of milling, intermixing and comminution effects are predominant, together with the introduction of a high concentration of defects in the Mg and Ni lattices. This effect is evidenced by a broadening of the diffraction profiles due to the decrease

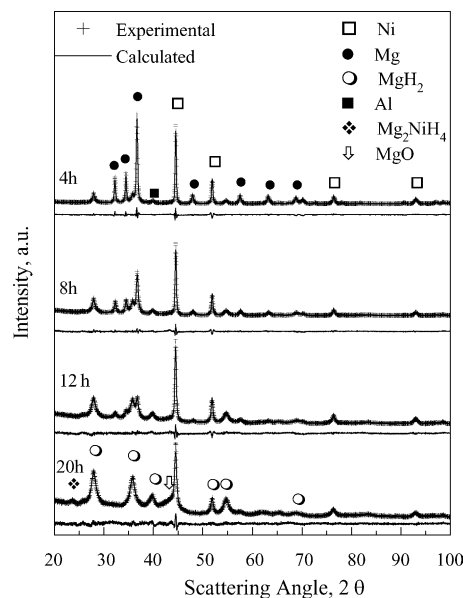


Fig. 1. X-ray diffraction patterns (+) and calculated profiles (line) of the sample Mg<sub>87</sub>Ni<sub>10</sub>Al<sub>3</sub> milled 4, 8, 12 and 20 h under H<sub>2</sub> atmosphere. The errors, calculated as a difference between the experimental and the calculated data, are reported in the bottom of each diffraction pattern.

of the average crystallite size and the increase of the lattice strain. Moreover, the dissolution of Al in the Mg lattice is observed as testified by the decreasing of the Mg cell parameters from  $a = 0.32096$  nm and  $c = 0.52112$  nm (not-milled), to  $a = 0.31972$  nm and  $c = 0.51938$  nm (milled 12 h). In addition, a broadening of the peaks of the MgH<sub>2</sub> phase was detected corresponding to a decrease of the crystallite size from 24 nm (4 h of milling) to 8 nm (16 h of milling). This value does not change upon further milling attesting that a saturation value for the crystallite size is reached. This result is in agreement with that reported by Hanada et al. [10].

#### 4. Thermal behavior

The thermal stability of the hydride formed by milling for different times was studied by DSC and TG measurements. The amount of hydrogen in the alloy was also determined. In Fig. 2a, the DSC curves of the samples milled 4, 8, 12 and 20 h are reported. For comparison, the DSC curve of nanocrystalline MgH<sub>2</sub> synthesised by reactive ball milling of Mg in H<sub>2</sub> atmosphere, at the same milling conditions, is also presented. As can be observed, the decomposition temperature of MgH<sub>2</sub> obtained in this study is considerably lower than that of pure nanocrystalline MgH<sub>2</sub>. Indeed, while for the sample without any metal addition the onset and the peak temperatures are ~300 and ~390 °C, respectively, in the case of the samples milled with Ni and Al different thermal behaviours were observed, as the milling time was increased. For the samples milled for 4, 8 and 12 h the onset temperatures are between 210 and 215 °C and the peak temperatures between 230 and 250 °C. After 16 h of milling, a hydride phase with

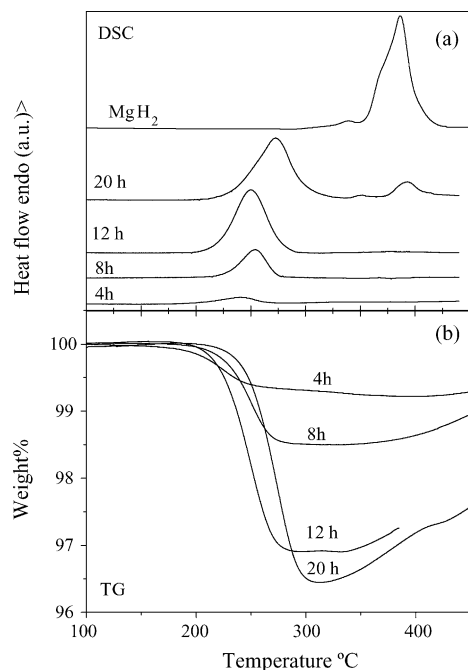


Fig. 2. (a) DSC curves (10 K/min) of the samples milled 4, 8, 12 and 20 h under hydrogen. For comparison the curve relevant to MgH<sub>2</sub> obtained by milling of Mg under H<sub>2</sub> is also reported. (b) TG curves (10 K/min) obtained after milling for 4, 8, 12 and 20 h.

slightly higher stability is formed and two transitions in the DSC curves can be observed. At longer milling time (20 h), a new peak at higher temperature appears. The nature of this second transition is currently under study.

From the results and taking in account that the formation of Mg<sub>2</sub>NiH<sub>4</sub> is observed only for the higher milling time, it can be assumed that the reduction of the desorption temperature may be due to the catalytic effect of the Ni in the mixture and possibly the Al dissolved in the Mg matrix. As observed from the X-ray diffraction analyses (not presented here) performed on the samples after heating treatments, more than one process is involved (such as the decomposition of the hydrides and the reaction between Mg and Ni to form of Mg<sub>2</sub>Ni) which contributes to the phenomena observed.

The hydrogen content in the alloy was determined by TG analyses showed in Fig. 2b. As expected the hydrogen amount increases with the milling time and a maximum value of about 3.5 wt.%, after 20 h of milling, was obtained. This value is lower than the theoretical capacity of the alloy (5.77 wt.%) and could be explained by the presence of MgO. The results obtained by thermo-gravimetry analysis have been confirmed by studying the kinetics properties of the sample obtained after 20 h of mechanical treatment. In Fig. 3, the absorption and desorption curves are shown. The experiments were carried out at three different temperatures, 300, 250 and 230 °C, respectively. The maximum capacity of the alloy is the same as that obtained by TG measurements. Fast absorption–desorption kinetics were obtained for the temperatures studied. The maximum hydrogen absorption was reached in less than 2 min. On the other hand, as

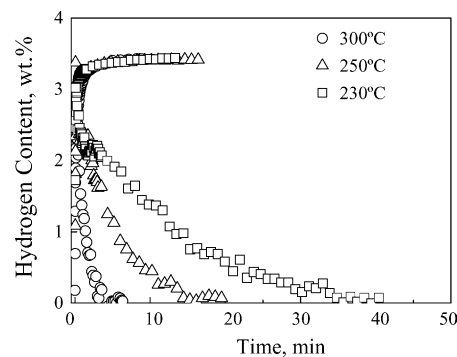


Fig. 3. Absorption–desorption kinetics curves, obtained at 300 °C (○), 250 °C (△) and 230 °C (□), of Mg<sub>87</sub>Ni<sub>10</sub>Al<sub>3</sub> mixture milled 20 h under hydrogen.

expected, pronounced differences in the desorption kinetics were obtained as the temperature decreased. At 300 °C total desorption was obtained in less than 5 min while at 250 and 230 °C 15 and 35 min were needed, respectively. These results are quite good considering the oxidation of the sample. Note that a MgO surface layer would negatively influence the absorption–desorption kinetics hindering the hydrogen diffusion into Mg nanograins. Probably, oxidation during milling leads to a fine dispersion of MgO particles, rather than to inactivation by a closed surface layer.

## 5. Conclusions

Reactive milling of an elemental Mg<sub>87</sub>Ni<sub>10</sub>Al<sub>3</sub> powder mixture under hydrogen atmosphere induces the synthesis of nanocrystalline MgH<sub>2</sub>. In the first stage of the milling, only β-MgH<sub>2</sub> was detected in the XRD diffraction patterns. When a high degree of conversion of Mg in the hydride was reached, the formation Mg<sub>2</sub>NiH<sub>4</sub> was observed. Increasing the milling time a structural refinement of hydride phase was observed together with the increase of disorder. A minimum value for the crystallite size of 8 nm was obtained. Small differences in the hydride stability were observed at different milling times. In spite of the oxidation of the sample, fast absorption–desorption kinetics were obtained.

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