

## Mg-Ni ALLOYS FOR HYDROGEN STORAGE OBTAINED BY BALL MILLING

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**Abstract**—The effect of the atmosphere and milling time on the structural, morphological and hydrogen reactivity properties of the mechanically alloyed Mg-Ni system is studied. Nanocrystalline Mg<sub>2</sub>Ni formed by ball milling in argon exhibits a higher thermal stability than the metals amorphized by milling during shorter times. It is shown that the initially fast hydrogen absorption kinetics of Mg<sub>2</sub>Ni at 250°C strongly depends on the crystallinity degree. When the Mg-Ni mixture is mechanically alloyed under hydrogen atmosphere, MgH<sub>2</sub> is formed at first and Mg<sub>2</sub>NiH<sub>4</sub> is obtained later. Samples prepared in argon show a higher hydrogen absorption capacity than those obtained in hydrogen.

**Keywords**—Mg-Ni, metallic hydrides, mechanical alloying, hydrogen absorption.

### I. INTRODUCTION

In the last years, several studies related with mechanically alloyed materials useful for hydrogen storage have been reported. This technique allows obtaining intermetallic compounds that react with hydrogen in a reversible process. In this way, the properties of the materials related with their surface, their particle size and the density of defects are important factors to be considered to improve the rate of the reaction with hydrogen (Abdellaoui *et al.*, 1999; Huot *et al.*, 1995; Liang *et al.*, 1998; Orimo *et al.*, 1997). In particular, there are several works on the Mg-Ni system that analyze the product of the mechanical alloying from pure metals (Huot *et al.*, 1995; Liang *et al.*, 1998), the effect of milling parameters on the formation of the Mg<sub>2</sub>Ni intermetallic compound (Orimo *et al.*, 1997; Tessier *et al.*, 1998) and also the characterization of the reaction with hydrogen.

In this paper we study the effect of milling time on the thermodynamics and the structural proper-

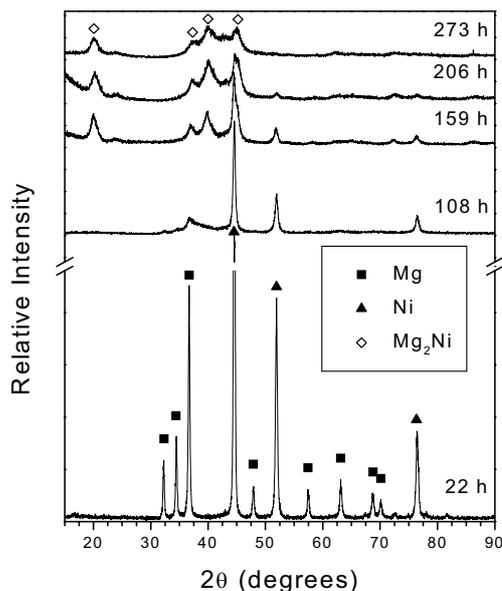
ties of Mg-Ni mixtures (2:1 atomic proportion) prepared under argon or hydrogen atmospheres. The hydrogen reaction kinetics is also analyzed.

### II. EXPERIMENTAL

Mechanical alloying of Mg-Ni mixtures was performed in a Uni-Ball-Mill-II (Australian Scientific Instruments) apparatus, using ferromagnetic steel balls as milling media and an external magnetic field controlling the movement of balls.

Mg granules (purity higher than 99.9%) and Ni powder (purity higher than 99.9%) in the atomic proportion 2:1 were placed in the milling chamber in the argon atmosphere of a glove box. The ball to powder weight ratio used was 18:1. The milling was performed in two atmospheres: argon (purity 99.995%) at a pressure of 0.1 MPa or hydrogen (purity 99.995%) at a pressure of 0.5 MPa. Samples of the product of milling were taken from the chamber, opened in the argon glove box, at regular intervals of time. Their structures were studied by X-ray diffraction (XRD, PW 1710, Philips Electronic Instruments) using CuK<sub>α</sub> radiation and Ni filter, at 40 kV and 30 mA. In order to investigate their thermal stability, samples milled during 108 and 273 hours were thermally treated at 200°C during 10 min under argon atmosphere. The thermal behavior of the samples was studied by differential scanning calorimetry (DSC 2910, TA Instruments) at a heating rate of 25°C min<sup>-1</sup> and an argon flow rate of 18 ml min<sup>-1</sup>. The total hydrogen content was determined by fusion and decomposition (LECO RH-404). Scanning electron microscopy (SEM 515, Philips Electronic Instruments) and energy dispersive X-ray analysis (EDX) were used to observe the microstructure.

The samples were placed in a closed system with constant volume under pure hydrogen atmosphere (99.995%) to study the hydrogen absorption kinetics. They were kept in vacuum at 250°C dur-



**Fig. 1:** XRD patterns of Mg-Ni milled under argon atmosphere for different milling times.

ing 5 hours before the first absorption. The hydrogen initial pressure was set to 4 MPa. The amount of absorbed hydrogen was estimated from the decrease of pressure with time.

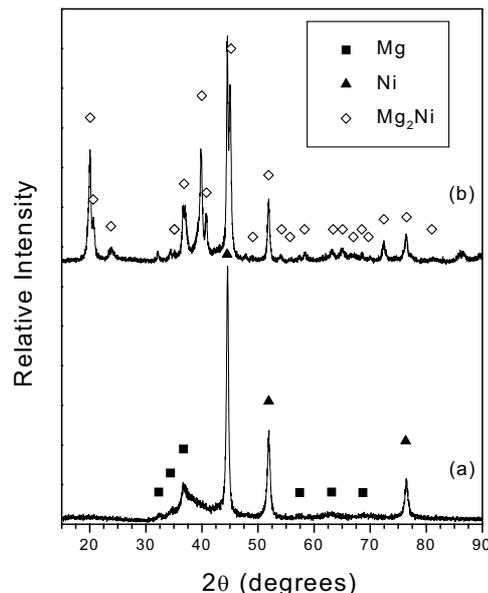
The successive hydrogen absorption/desorption kinetic measurements were performed at 250°C (absorption) and 300°C (desorption).

### III. RESULTS

#### A. Samples milled in argon

The structural evolution of the Mg-Ni mixture milled in argon is shown in Fig. 1. During the initial period of milling (22 h) the XRD diagram corresponds to both metals used as starting materials (Mg: JPCDS Powder Diffraction Data Card N° 35-821, Ni: JPCDS Powder Diffraction Data Card N° 4-850). Amorphization of magnesium is observed after 108 h and the intermetallic  $Mg_2Ni$  (JPCDS Powder Diffraction Data Card N° 35-1225) is detected after 159 h of milling. This compound shows a nanocrystalline structure with the half height width of its peaks increasing with milling time, indicating the reduction of the crystallite size.

To analyze the thermal stability of the phases, two samples milled during 108 and 273 h respectively were thermally treated at 200°C in argon. While crystallization of  $Mg_2Ni$  is observed by XRD in the first sample (Fig. 2), the nanocrystallinity of the sample milled for the longer time remains unchanged. The microstructural study of the sample milled 108 h shows that the size of ag-



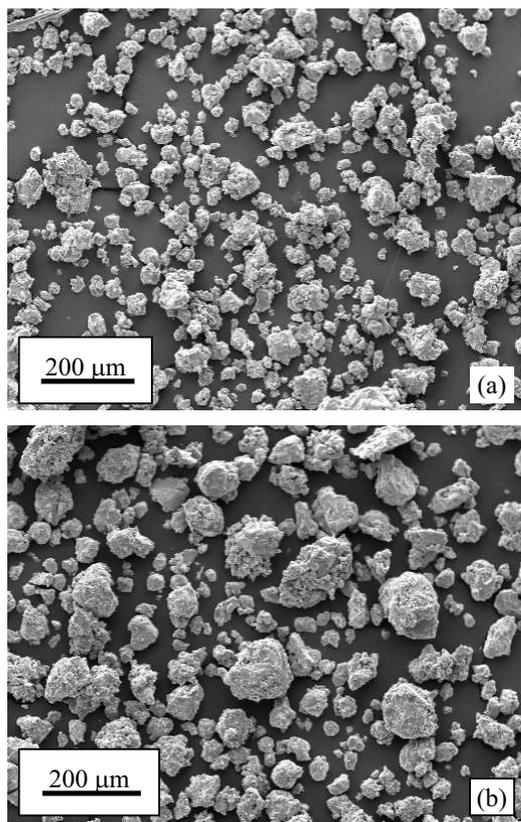
**Fig. 2:** XRD of a sample milled 108 h in argon (a) before and (b) after thermal treatment at 200°C.

glomerates increases with thermal treatment (Fig. 3), while the EDX analysis indicates that the distribution of the metals inside the particles is homogeneous and close to the initial atomic ratio.

#### B. Samples milled in hydrogen

The evolution of the X-ray diffractograms with milling time for samples milled under hydrogen atmosphere is shown in Fig. 4.  $\beta$ - $MgH_2$  (JPCDS Powder Diffraction Data Card N° 12-697) is formed during the first hours of milling while Mg and Ni are still detected after 22 h of milling. The amount of  $\beta$ - $MgH_2$  increases with milling up to 71 h, being consumed by reaction with nickel for longer milling times. In fact, after 159 h the presence of  $Mg_2NiH_4$  is observed. The broadening of the peaks associated to the intermetallic hydride indicates its nanocrystalline state. After 273 h of milling XRD shows that this compound is still mixed with Ni. Magnesium that did not react with nickel has been amorphized by the milling.

Figure 5 shows DSC measurements of samples milled under hydrogen atmosphere during 71 and 273 h. The first sample shows an endothermic peak at 416°C assigned to  $\beta$ - $MgH_2$  decomposition in agreement with previous thermal studies (Hout *et al.*, 1995; Zaluski *et al.*, 1995). For the sample milled 273 h we identify an endothermic peak at 305°C and two exothermic peaks at 360°C and 438°C. The endothermic event is attributed to  $Mg_2NiH_4$  decomposition (Selvam *et al.*, 1988) and the exothermic peaks at 360 and 438°C correspond



**Fig. 3:** SEM micrographs of a sample milled 108 h in argon (a) before and (b) after thermal treatment.

to the crystallization of the compounds  $Mg_2Ni$  and  $MgNi_2$ , respectively (Yamamoto *et al.*, 1999).

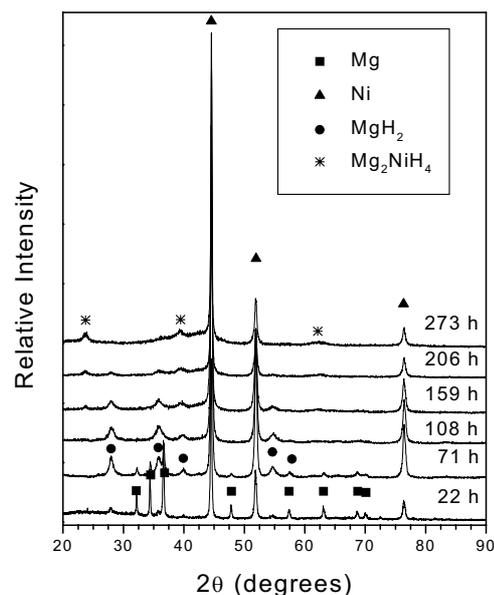
Thermogravimetric analysis of samples milled 273 h shows a weight loss of 2.6 wt.% associated to the intermetallic hydride decomposition peak. This value is in good agreement with the hydrogen content determined by LECO.

### C. Hydrogen absorption kinetics

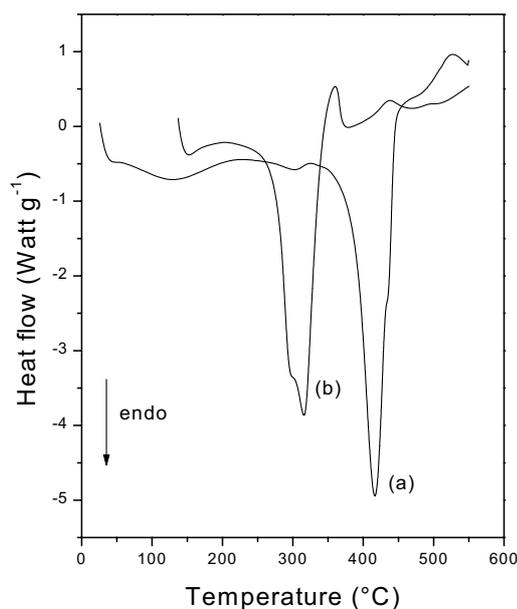
To evaluate the potential use of these alloys for hydrogen storage, the absorption kinetics of samples milled 273 h under both atmospheres was studied.

Samples obtained by milling in argon do not react with hydrogen in the experimental conditions stated in section II. However, after the thermal treatment in vacuum, hydrogen absorption is observed for these samples.

Figure 6 shows the absorption curves measured at 250°C with samples milled in hydrogen or milled in argon and then thermally treated. The maximum hydrogen absorption capacity was achieved for samples milled in argon (2.6 wt.%), much higher than that determined for samples milled in hydrogen (0.8 wt.%).



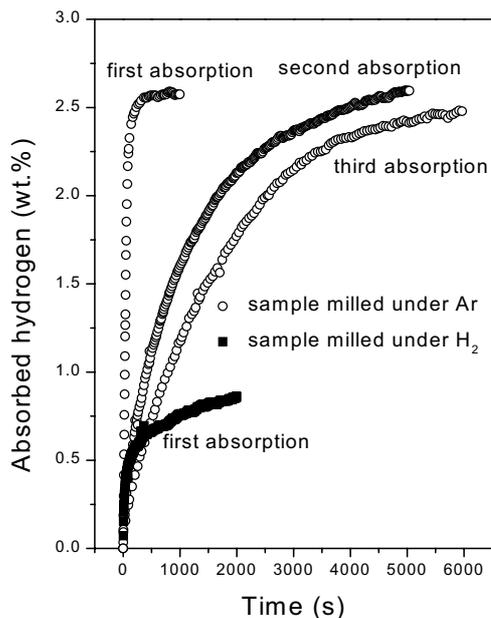
**Fig. 4:** XRD patterns of Mg-Ni milled in hydrogen after different milling times.



**Fig. 5:** DSC curves of samples milled in hydrogen during (a) 71 and (b) 273 hours.

To analyze the variation of hydrogen storage capacity with the thermal treatments and absorption/desorption cycles, we examined the different phases present in the samples by XRD. Figure 7 shows the XRD patterns corresponding to the sample milled for 273 h in argon:

- thermally treated at 250°C in vacuum during 5 h (curve “a”),
- after the first absorption/desorption process (curve “b”),
- after the second absorption/desorption cycle



**Fig. 6:** Hydrogen absorption curves at 250°C of samples milled during 273 h under argon or hydrogen atmospheres.

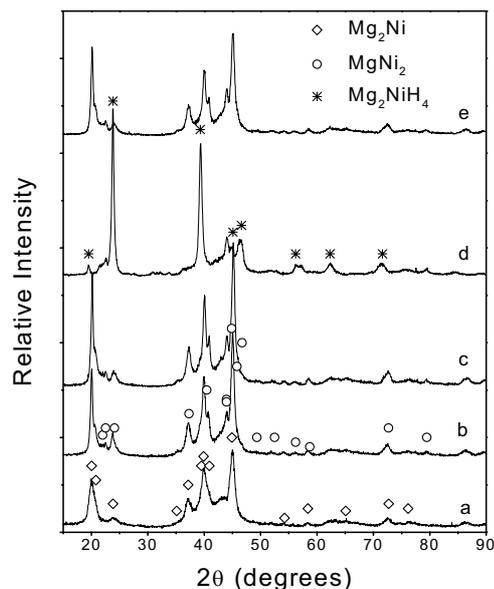
- (curve “c”),
- after the third hydrogen absorption (curve “d”),
- after finishing the hydrogen desorption stage (curve “e”).

Crystallization of the  $Mg_2Ni$  intermetallic phase is enhanced by the initial thermal treatment in vacuum, as it can be observed by comparison of Fig. 1 and Fig. 7 (curve “a”). After hydrogen absorption/desorption cycles this phase, initially nanocrystalline, increases its degree of crystallinity, as observed in Fig. 7 (curve “e”). The appearance of the  $MgNi_2$  compound after the first interaction with hydrogen is a remarkable event. Its formation was also observed in the DSC analysis (see Fig. 5). However it is not undoubtedly clarified if it is formed during the absorption or the desorption process.

Samples analyzed by XRD after the third hydrogen absorption show patterns corresponding to the hydride phase  $MgNi_2H_4$  and unreacted  $MgNi_2$ .

#### IV. DISCUSSION

The above results show that the milling of Mg and Ni under argon atmosphere leads to the formation of the intermetallic  $Mg_2Ni$  after long periods of milling time. The material progressively decreases its crystallite size due to fracture of the particles produced by the high-energy impacts of the balls. The crystallite size was determined using the Scherrer equation (Klug and Alexander, 1974):



**Fig. 7:** Structural evolution of the sample milled for 273 h in argon after reaction with hydrogen.

$$\beta = \frac{C \lambda}{d_c \cos \theta} \quad (1)$$

where  $\beta$  is the broadening of the diffraction peak due purely to crystallite size measured at half of its maximum intensity,  $C$  is a constant which mainly depends on the crystallite shape and it is taken equal to 0.9,  $\lambda$  is the radiation wavelength,  $d_c$  is the crystallite size and  $\theta$  is the diffraction angle. The values obtained for samples milled during 159, 206 and 273 hours were 85, 64 and 51 Å, respectively.

The material obtained by milling during 273 h presents low reactivity to crystallization. As a result of the accumulation of stresses during milling and the defects created on the powder surfaces, the material milled for longer times preserves its nanocrystalline structure after thermal treatment at 200°C. A slight increase in crystallinity is produced after the treatment performed at 250 °C during 5 h. On the other hand, although the formation of  $Mg_2Ni$  by mechanical alloying was not observed after 108 h of milling, the crystallization of this compound is achieved by thermal treatment at a lower temperature than that reported in the literature (Yamamoto *et al.*, 1999). The presence of a precursor of  $Mg_2Ni$  in a ball milled mixture of Mg and Ni was previously reported by S. Ordóñez *et al.* (1999).

Metallic magnesium presents low reactivity with hydrogen. From the obtained value for the decomposition heat observed by DSC and using available data of the formation enthalpy (Kubaschewski and Alcock, 1979), it was calcu-

lated that only 36 wt.% of the magnesium used in the initial mixture had reacted with hydrogen after 71 h of milling. When comparing the results from both milling atmospheres studied in this work, we observe that unreacted metals remain present in the mixture milled in hydrogen while the reaction has been completed if milling is performed in argon for the same time. Heterogeneous reactions are observed when mechanical alloying is performed under reactive atmosphere ( $H_2$ ); here the synthesis of hydrides is favored, instead of the formation of the intermetallic  $Mg_2Ni$ . After 273 h of milling the total hydrogen content is 2.6 wt.% (lower than the theoretical value of 3.6 wt.% for  $Mg_2NiH_4$ ). The material presents free nickel (Fig. 4), unreacted amorphous magnesium and magnesium-nickel hydride. The splitting of the endothermic peak in the DSC analysis corresponding to the decomposition is attributed to the presence of a mixture of hydrides:  $Mg_2NiH$  and  $Mg_2NiH_4$  (Selvam *et al.*, 1988).

The hydrogen absorption curves measured at 250°C corresponding to the sample milled in argon (Fig. 6) show that the  $Mg_2Ni$  phase, after partial crystallization by thermal treatment in vacuum at the same temperature, absorbs hydrogen readily, completing the process in about 500 s. Further absorption kinetics is slower. In particular, during the following absorption stage, the same hydrogen storage capacity is achieved at a time one order of magnitude higher than the initial one. This behavior can be related with the evolution of the material. During the first absorption the surface defects generated by the milling act as hydrogen pick up centers that allow faster hydrogen entrance, diffusion and hydride nucleation with a higher specific volume than the host phase (Song, 1995). The importance of these defects is evident in the evolution of the material with the hydrogen absorption/desorption cycles. After the first desorption stage at 300°C crystallization of  $Mg_2Ni$  and  $MgNi_2$  intermetallics is observed.  $Mg_2Ni$  shows a noticeable increment in crystallite size in relation with the same phase before the first absorption. A diminution in the amount of defects leads to reduction of the hydrogen absorption rate. Free magnesium is observed in the material due to the formation of  $MgNi_2$  from the Mg-Ni hydride. Although it was reported that an improvement in hydrogen absorption kinetics is observed when the ratio  $Mg_2Ni/Mg$  increases (Liang *et al.*, 1998), the influence of defects masked this effect in our experiments. Moreover, the hydrogen absorption kinetics is slower after successive absorption/desorption cycles due

to this structural reconstitution of the material. It should be pointed out that hydrogen absorption was measured at a temperature higher than the temperature of monoclinic to cubic  $Mg_2NiH_4$  transformation and it has been reported (Zaluski *et al.*, 1995) that  $Mg_2Ni$  hydride formation is easier in this condition. However, the total hydrogen content of the material in our measurements is lower than the maximum absorption capacity of the system.

For samples milled under hydrogen atmosphere the final hydrogen content is lower than that observed in samples milled in argon. Here, the explanation lies on the proportion of the intermetallic  $Mg_2Ni$  available for the hydriding process. Both, the presence of free metals in the sample and an incomplete desorption stage prior to the measured absorption can be the reasons.

Now we are developing further studies to investigate the precise conditions under which the  $MgNi_2$  phase is formed and the influence of successive absorption/desorption cycles on the reaction kinetics.

## V. CONCLUSIONS

$Mg_2Ni$  is obtained by ball milling under argon atmosphere and this intermetallic compound retains its nanocrystalline state also after a thermal treatment at 200°C. When milling is performed under reactive atmosphere (hydrogen), heterogeneous reactions like hydride formation take place. During mechanical alloying the material evolves from the mixture of metals to  $MgH_2$ , that is initially synthesized, and to  $Mg_2NiH_4$ , which is formed during longer milling times. While milling in argon generates the complete reaction of Mg and Ni, unreacted metals are present still in the material milled under hydrogen atmosphere during the same period of time.

The sample milled in argon absorbs hydrogen readily at 250°C during the first absorption stage. Subsequent reaction with hydrogen is slower and this behavior is related with structural and microstructural changes occurring to the material in the absorption/desorption cycles.  $MgNi_2$  is formed and  $Mg_2Ni$  increases its crystallinity after the first desorption stage, favoring the diminution of the hydrogen absorption rate. Samples milled in argon show a higher hydrogen absorption capacity than the samples milled in hydrogen.

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Received: May 11, 2001.

Accepted for publication: June 7, 2002.

Recommended by Subject Editor A. L. Cukierman and Guest Editors E. L. Tavani and J. E. Perez Ipiña.