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Journal of Alloys and Compounds 356–357 (2003) 438–441

Journal of ALLOYS AND COMPOUNDS

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Enhancement of hydrogen storage in MgNi by Pd-coating

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Received 15 July 2002; received in revised form 26 August 2002; accepted 1 September 2002

Abstract

MgNi alloys prepared by mechanical alloying were coated with Pd nanoparticles via a polyol process. Such a process allows the deposition of fine particles of metal catalysts on the MgNi alloy surface. This surface modification leads to a strong improvement of the H storage performances of the alloy. The hydrogen release at 150 °C increases from 0.6 wt.% for uncoated MgNi alloy to 1.5 wt.% for a 5 wt.% Pd-coated MgNi alloy. The strong enhancement of the desorption capacity probably results from the catalytic effect of Pd, which may act as a hydrogen pump, thus favoring hydrogen migration from the bulk to the surface of the alloy.

Keywords: Amorphous materials; Hydrogen storage materials; Mechanical alloying; Grain boundaries

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1. Introduction

For mobile applications, hydrogen is the ideal fuel because it is lightweight, highly abundant and its oxidation leads to an environmentally safe product (water). Hydrogen storage, however, remains a great challenge. Among many metals exhibiting a reversible hydridation, magnesium is one of the most promising, due to its low cost and to its high hydrogen storage capacity (7.6% by weight). But, its practical use remains limited because of slow desorption kinetics below 600 K.

In recent years, Mg hydriding/dehydriding properties have been significantly improved by alloying Mg with other metals, especially with Ni. Mechanical alloying (MA), involving a solid state process at room temperature, appears to be one of the most powerful techniques to produce MgNi alloys [1,2]. Moreover, within the field of hydrogen absorption/desorption, the production of nanocrystalline and/or amorphous alloys by MA is relevant. Indeed, the nanocrystalline nature improves the hydrogen sorption properties, due to enhanced hydrogen absorption and diffusion along the grain boundaries [3].

A critical factor for hydrogen sorption is the metal surface, which should be able to dissociate the H_2 molecules and to allow easy diffusion of hydrogen atoms into the bulk. A promising way to tune the hydride forming alloy surface is the deposition of nanoparticles of metals well known as good hydrogen catalysts (Ni, Pd, and Pt). In this paper, metal nanoparticles are deposited on ball-milled MgNi alloys using a chemical process. This process (namely the polyol process) involves the reduction of a metallic salt in a liquid polyol. Among several catalysts tested, the benefit of Pd on the hydrogen absorption/desorption performances of Mg–Ni alloys was by far the highest.

2. Experimental

MgNi alloys were prepared by MA using a SPEX model 8000 mill (shock interactions). Five grams of pure Mg and Ni powders (Alfa, <40 μm) were introduced in a 50-cc milling container in an argon-filled glove box; 12- and 14-mm diameter stainless steel balls were used and the ball to powder weight ratio was approximately 8. Milling times lasted from 20 to 60 h.

The crystalline structure of the ball-milled powders was assessed by means of X-ray diffraction using a Philips PW1470 diffractometer ($\lambda_{\mathrm{Cu\ K}\alpha} = 1.5418$ Å). The morphology of the alloys was observed by SEM (Philips XL30 FEG) coupled with a EDX spectrometer (Oxford ISIS) to determine the alloy chemical composition. The BET-specific surface area was measured by a Micromeritics Gemini

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doi:10.1016/S0925-8388(03)00115-4

II 2370 device, after preliminary outgasing at 100 °C for 2 h in order to remove physisorbed water.

Hydrogen sorption performances of the ball-milled powders were determined by a home built PCT apparatus based on a volumetric method. The absorbed hydrogen quantity was measured at different temperatures (up to 200 °C) with increasing hydrogen pressure up to 10 bars. Hydrogen desorption properties were determined in primary vacuum with increasing temperature up to 200 °C.

3. Results

3.1. Synthesis of MgNi alloys by MA

Our work has been focused on $Mg_{100-x}Ni_x$ alloys prepared by MA with a special interest for the $Mg_{50}Ni_{50}$ composition. Fig. 1a displays the evolution in crystallinity of a ball-milled MgNi alloy versus milling time. The diffractograms exhibit mainly two broad peaks located around 22° and 44°; the symmetry of the latter increasing with milling time. This peak is significantly asymmetric in the case of the 20-h ball-milled sample, suggesting the overlapping of two broad features, whereas these two contributions become indistinguishable in the 60-h ball-milled powder. This trend emphasizes the important amorphization of the alloy.

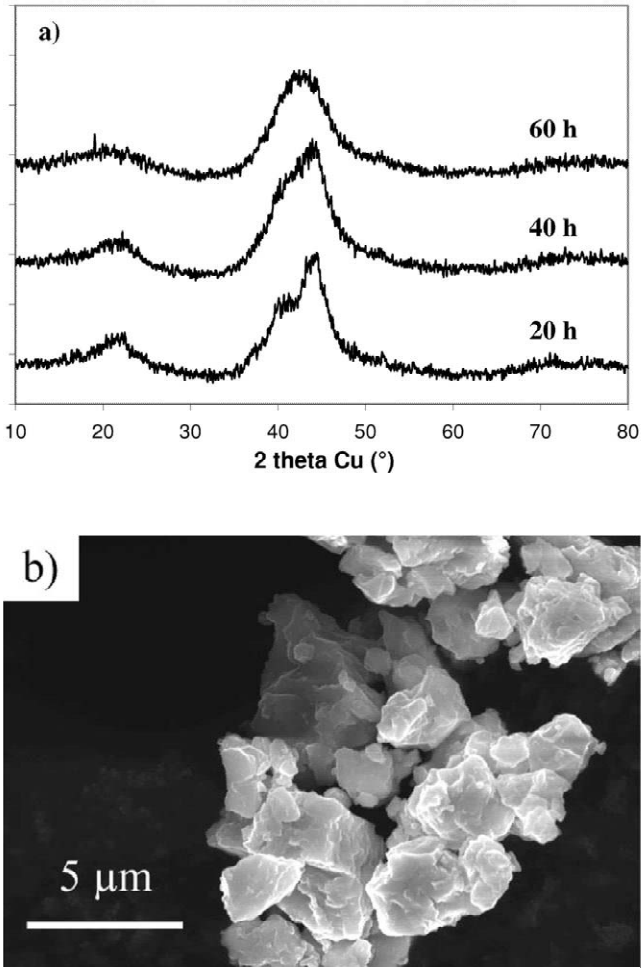

Fig. 1. Evolution of XRD diagrams versus milling time (a) and SEM micrograph (b) of ball-milled MgNi alloy.

Preliminary TEM studies show that whatever the milling time, electronic diffraction patterns are typical of nanocrystalline powders with dotted rings identified as Mg_2Ni and $MgNi_2$. Crystallites with a 10–15-nm length are observed. At this stage, it remains difficult to conclude on the nanometric scale organization and microstructure of the MgNi alloy: real amorphous MgNi or coexistence of Mg_2Ni and $MgNi_2$ nanodomains. XRD at various temperatures reveal an important recrystallization of the alloy above 250 °C. At higher temperature, sharp reflections of well-crystallized Mg_2Ni and $MgNi_2$ phases coexist [4].

The 40-h ball-milled sample exhibits a particle size in the 1–5-μm range (cf. Fig. 1b). EDX spectroscopy indicates that the sample is homogeneous in composition with a Mg/Ni ratio close to one with a slight iron contamination that remains less than 2 wt.%. In agreement with the micrometer particle size observed by SEM, a low BET-specific surface area in the order of 0.6 m^2/g was measured. Longer milling times do not decrease the average particle size of the powder.

The H absorption of ball-milled MgNi alloys was measured at 150 °C. For milling times higher than 20 h, the H uptake remains close to 1.5–1.6 wt.% under a 10-bar hydrogen pressure. On the contrary, milling time drastically modifies the quantity of hydrogen released. For the 20-h ball-milled powder, the desorption is very limited (less than 0.4 wt.% at 200 °C), whereas it reaches 0.6 wt.% at 150 °C for the 40- and 60-h ball-milled alloys. This improvement is ruled by an increase in internal strain and grain boundaries that enhances hydrogen diffusion. Thus, the 40-h ball-milled sample was chosen as starting and reference powder for Pd nanoparticles deposition.

3.2. Pd-coating by the polyol process

With the aim of promoting H desorption through surface modification, chemical coating of the ball-milled MgNi alloy was pursued using the polyol process. This process involves the reduction of metallic salts in a liquid polyol allowing to precipitate metallic nanoparticles in solution or onto a substrate [5,6]. Previous to the metal deposition step, the reactivity of MgNi alloy in several solvents was studied. Ethylene-glycol (EG, CH_2OHCH_2OH) was chosen, due to the absence of brucite formation on the alloy surface.

Among several hydrogen catalysts (Ni, Pd, Pt, etc.), Pd has been clearly identified in the literature as the metal additive leading to a significant enhancement of the hydrogen storage performances of MgNi alloys [7]. Therefore, it was selected for the present study. The Pd

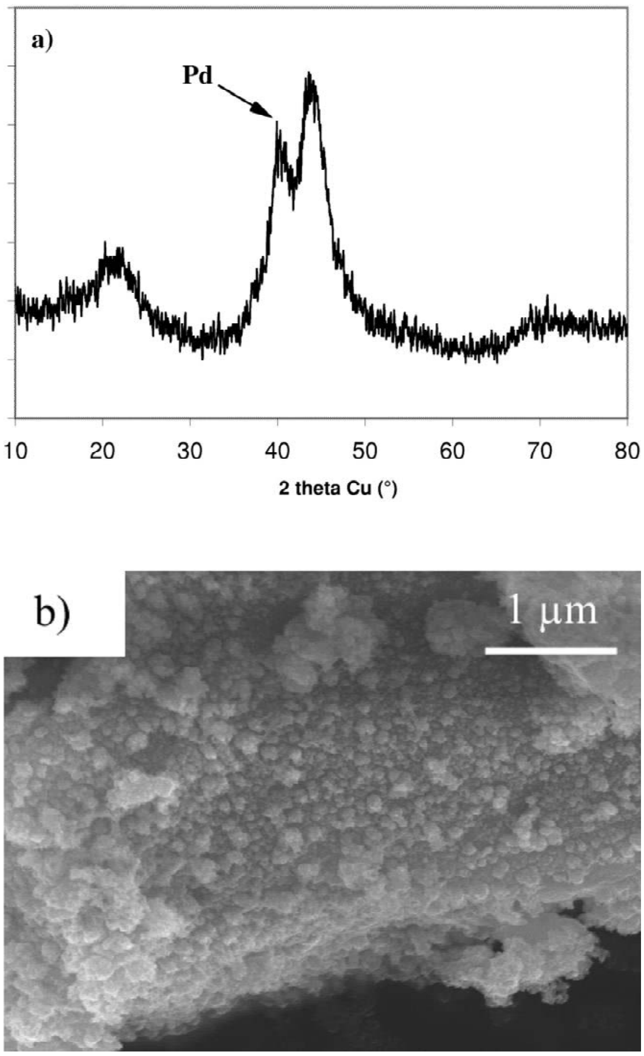

Fig. 2. XRD diagram (a) and SEM micrograph (b) of 5 wt.% Pd-coated MgNi alloy.

precursor for the polyol process was Pd nitrate [$Pd(NO_3)_2$, $2H_2O$] and the reduction was carried out at ambient temperature in EG. After the reaction was complete, the Pd coated-powder was washed three times with acetone.

The XRD diagram of a 5 wt.% Pd-coated MgNi powder is shown in Fig. 2a. The appearance of a broad peak at 40° reveals the presence of fine Pd particles (111 reflection) with an average particle size in the 50–100 nm range (cf. Fig. 2b). EDX spectroscopy confirms that the Pd content is equal to 5% by weight and shows that the Pd particles are randomly dispersed on the micronic particles of the MgNi alloy. Low C and O quantities, due to the presence of remaining EG and its derivatives, are also detected by EDX spectroscopy.

Hydrogen absorption is slightly increased by Pd-deposition: from 1.6 to 1.8 wt.% under 10 bars at 150 °C (cf. Fig. 3a). The corresponding desorption curves (H release versus temperature) are presented in Fig. 3b. The beneficial effect of Pd is remarkable, because a strong improvement of the H release is noticed. For the 5 wt.% Pd-coated MgNi alloy, 1.5 wt.% H is released at a temperature as low as 150 °C, for which the starting alloy presents a low desorption (around 0.6 wt.%).

The strong Pd activity on hydrogen desorption was somewhat unexpected, since its role as catalyst is usually expected in hydrogen absorption [7]. The solid–gas interface is strongly activated by the Pd-coating. During hydrogen desorption, Pd particles dispersed on the MgNi alloy surface act as ‘hydrogen pumps’ and therefore, accelerate H migration and H diffusion from the bulk to the surface of the ball-milled MgNi alloy, via the grain boundaries. Further enhancement of the H desorption, through modification of the MgNi/Pd interface, is currently under investigation. Preliminary results show that a short extra-grinding period (3 h) of the polyol reactional mixture (5 wt.% Pd coated MgNi+EG) slightly improves

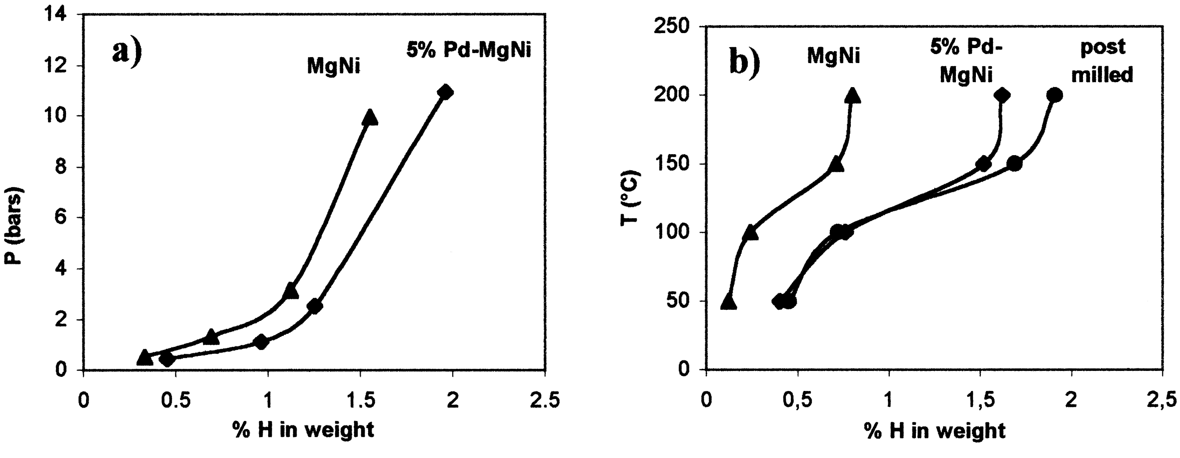

Fig. 3. Improvement of the H sorption properties of a Mg Ni alloy by Pd-coating (a) absorption at 150 °C, (b) desorption under primary vacuum.

the H release (close to 2 wt.% at 200 °C) (cf. Fig. 3b), probably due to precipitation of Pd particles at the grain boundaries of the ball-milled MgNi alloy.

4. Conclusions

Pd nanoparticles were deposited via the polyol process on the MgNi alloys prepared by mechanochemistry. This process, involving chemical reduction of a metallic salt, allows to disperse fine Pd particles onto the surface of the alloy. The strong increase in H desorption (from 0.6 to 1.5 wt.% at 150 °C for uncoated and 5 wt.% Pd-coated MgNi alloy, respectively) is attributed to a catalytic effect of Pd, which may act as a hydrogen pump thus favouring hydrogen migration from the bulk to the surface of the alloy. Improvement of the reactivity of the MgNi/Pd interface by mechanical grinding under hydrogen is currently in progress.

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