

HYDROGEN STORAGE BY Mg-BASED NANOMATERIALS

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Abstract. In this work, we have studied experimentally the structure and electrochemical properties of nanocrystalline $Mg_{2-x}Al_xNi$ - and nanocomposite $Mg_{2-x}Al_xNi/Pd$ -type hydrogen storage materials ($x=0, 0.5$). These materials were prepared by mechanical alloying (MA) followed by annealing (450 °C/0.5 h). In the nanocrystalline Mg_2Ni powder, discharge capacity up to 100 mA h g⁻¹ was measured. It was found that aluminium substituting magnesium in $Mg_{2-x}Al_xNi$ alloy greatly improved the discharge capacity of studied material. In nanocrystalline $Mg_{1.5}Al_{0.5}Ni$ powder, discharge capacities up to 175 mA h g⁻¹ were measured. On the other hand, mechanically coated Mg-based alloys with palladium have effectively reduced the degradation rate of the studied electrode materials.

1. INTRODUCTION

The ZrV_2 , $LaNi_5$ and $TiNi$ phases are familiar materials which absorb large quantities of hydrogen [1-3]. These types of hydrogen forming compounds have recently proven to be very attractive as negative electrode material in rechargeable nickel-metal hydride batteries. Magnesium-based hydrogen storage alloys have been also considered to be possible candidates for electrodes in Ni-MH batteries [3-5].

Conventionally, the microcrystalline hydride materials have been prepared by arc or induction melting and annealing. However, either a low storage capacity by weight or poor absorption-desorption kinetics in addition to a complicated activation procedure have limited the practical use of metal hydrides. Substantial improvements in the hydriding-dehydriding properties of metal hydrides could be possibly achieved by the formation of nanocrystalline structures by non-equilibrium processing technique such as mechanical alloying (MA) [5-8]. The raw materials used for MA are avail-

able commercially as high purity powders that have sizes in the range of 1-100 μm. During the mechanical alloying process, the powder particles are periodically trapped between colliding balls and are plastically deformed. Such feature occurs by the generation of a wide number of dislocations as well as other lattice defects. Furthermore, the ball collisions cause fracturing and cold welding of the elementary particles, forming clean interfaces at the atomic scale. Further milling leads to an increase of the interface atom number and the sizes of the elementary component area decrease from millimeter to submicrometer lengths. Concurrently to this decrease of the elementary distribution, some nanocrystalline intermediate phases are produced inside the particles or at its surfaces. As the milling duration develops, the content fraction of such intermediate compounds increases leading to a final product whose properties depend on the milling conditions.

Recently, it has been shown that MA of Mg_2Ni is effective for the improvement of the initial hydro-

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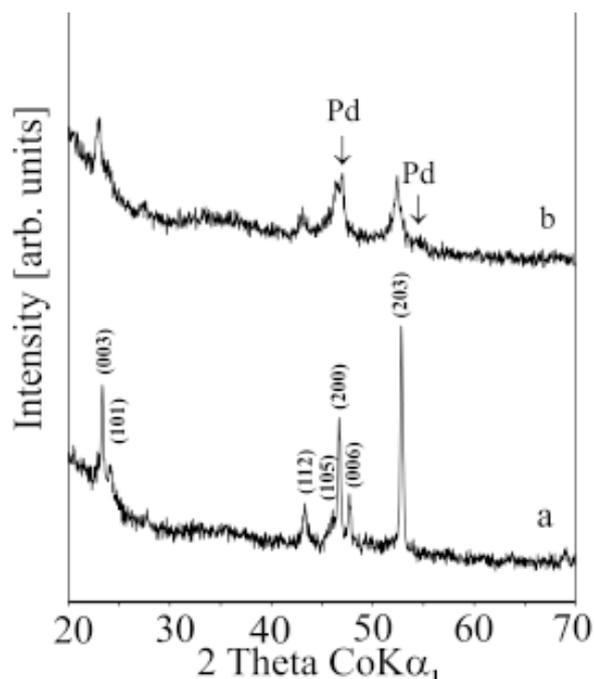


Fig. 1. XRD spectra of nanocrystalline Mg₂Ni- and nanocomposite Mg₂Ni/Pd-type hydrogen storage materials produced by mechanical alloying followed by annealing (see text for details).

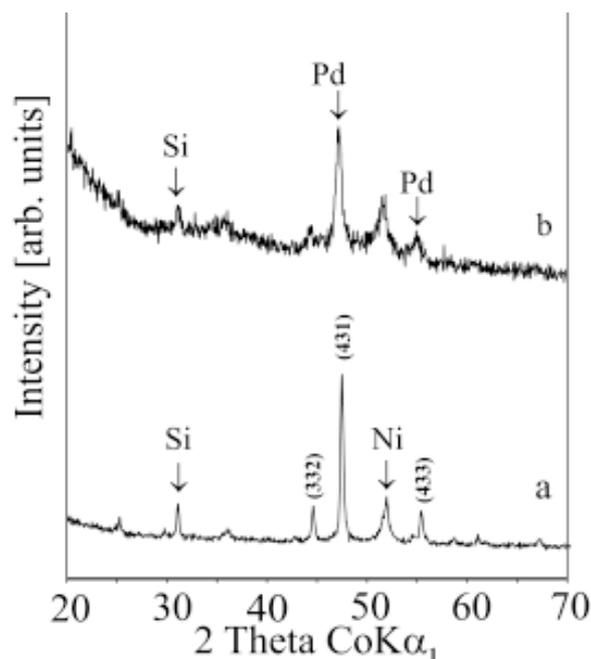


Fig. 2. XRD spectra of nanocrystalline nanocrystalline Mg_{1.5}Al_{0.5}Ni- and nanocomposite Mg_{1.5}Al_{0.5}Ni/Pd-type hydrogen storage materials produced by mechanical alloying followed by annealing (see text for details).

gen absorption rate, in comparison to microcrystalline Mg₂Ni, due to the reduction in the particle size and to the creation of new clean surfaces [6]. Additionally, it was found that the partial substitution of magnesium by Al in Mg_{2-x}Al_xNi alloy, synthesized by mechanical alloying method, leads to an increase in discharge capacity and cycle life [5]. With increasing Al concentration in Mg_{2-x}Al_xNi alloy, the discharge capacity increases due to the increase of the amount of the CsCl-type cubic phase.

As a continuation of our earlier studies, in this work, we have synthesised nanocrystalline Mg_{2-x}Al_xNi- and nanocomposite Mg_{2-x}Al_xNi/Pd-type hydrogen storage materials ($x=0, 0.5$). The structural, thermodynamic and electrochemical properties of synthesized materials were studied.

2. EXPERIMENTAL DETAILS

The nanocrystalline Mg_{2-x}Al_xNi hydrogen storage materials ($x=0, 0.5$) were prepared using mechanical alloying followed by annealing treatment. Mechanical alloying was performed under an argon

atmosphere using a SPEX 8000 Mixer Mill. The round bottom stainless vials were used. The high purity elemental powders (Mg $\leq 44 \mu\text{m}$, Ni 3-7 μm and Al $\leq 75 \mu\text{m}$) were mixed and loaded into the vial in the glove box (Labmaster 130) containing an argon atmosphere ($\text{O}_2 \leq 2 \text{ ppm}$ and $\text{H}_2\text{O} \leq 1 \text{ ppm}$). In both cases an extra 8 wt.% of magnesium was used. The mill was run up to 80 h for every powder preparation. The as-milled Mg₂Ni powders were heat treated under high purity argon to induce the form ordered phases. The powders were examined by XRD analysis, using CoK α radiation, at various stages during mechanical alloying.

The MA and annealed Mg_{2-x}Al_xNi hydrogen storage materials were mixed with 10 wt.% Pd powder (74 μm , purity 99.9 %) and milled for 1 h in a SPEX Mixer Mill. The weight ratio of hard steel balls to mixed powder was 30:1. Finally, the treatment of 10 wt.% addition of Ni powder was done for all the materials subjected to electrochemical measurements as working electrodes [8]. Soaking of the electrodes in 0.01M NH₄F solution for 1 h at room temperature was sufficient for the initial activation.

Table 1. Structure, lattice parameters, crystallite sizes and discharge capacities for nanocrystalline $Mg_{2-x}Al_xNi$ - and nanocomposite $Mg_{2-x}Al_xNi/Pd$ -type hydrogen storage materials ($x=0, 0.5$).

| Material | Structure and lattice constants (Å) | d (nm) | Discharge capacity at 1st cycle (mA h/g) |
|---------------------------------------|--|----------|--|
| Nanocrystalline Mg_2Ni | hexagonal $a=5.216, c=13.246$ | 30 | 100 |
| Nanocrystalline $Mg_{1.5}Al_{0.5}Ni$ | cubic $a = 3.149$ | 25 | 175 |
| Nanocomposite Mg_2Ni/Pd | hexagonal/f.c.c. $a=5.254, c=13.435 / a=3.8907$ | 25 | 305 |
| Nanocomposite $Mg_{1.5}Al_{0.5}Ni/Pd$ | cubic/f.c.c. $a=3.171 / a=3.8907$ | 20 | 240 |

The constant current charge/discharge measurements were performed at current density of $i=4$ mA g^{-1} . A detailed description of the electrochemical measurements (initial activation, electrochemical pressure-composition (e.p.c.) isotherms for absorption and desorption of hydrogen and charge/discharge cycle tests in half Ni-MH cells) was given in Ref. [9].

3. RESULTS AND DISCUSSION

As cited above, nanocrystalline $Mg_{2-x}Al_xNi$ - and nanocomposite $Mg_{2-x}Al_xNi/Pd$ -type hydrogen storage materials ($x=0, 0.5$) have been prepared by a two step process: mechanical alloying followed by heat treatment (Figs. 1 and 2, Table 1). As it was shown in a previous work [5], in the case of $2Mg + Ni$ composition, the powder mixture milled for more than 90 h has transformed completely to the amorphous phase, without formation of other phase. Formation of the nanocrystalline Mg_2Ni alloy was achieved by annealing the amorphous material in high purity argon atmosphere at 450 °C for 0.5 h (Fig. 1a). All diffraction peaks were assigned to those of the hexagonal crystal structure with cell parameters $a=5.216$ Å, $c=13.246$ Å. In the case of $Mg_{1.5}Al_{0.5}Ni$, two phase composition was received (Fig. 2a): Ti_2Ni ($a=3.149$ Å) and nickel ($a=3.53$ Å). Table 1 reports the cell parameters of all the studied materials. The average crystallite sizes of the nanocrystalline Mg_2Ni and $Mg_{1.5}Al_{0.5}Ni$ powders, according to Scherrer analysis, were of the order of 30 nm and 25 nm, respectively.

In this work, the capacity of the alloy electrode in relation to the amount of absorbed hydrogen (wt.%) was calculated based on the input/output charge [10,11]. In accordance with the equation ($E_s = -0.9325 - 0.0291 \log p(H_2)/p_0$, where E_s is the rest potential of the (MH) electrode vs. the Hg/HgO/6M KOH reference electrode, $p(H_2)$ is the equilibrium pressure, and p_0 is the standard pressure), the charge of one order of magnitude in hydrogen pressure in the alloy results in a change in the electrode potential of 29 mV. The e.p.c. isotherms determined on the nanocomposite $Mg_{2-x}Al_xNi/Pd$ ($x=0, 0.5$) materials are illustrated in Fig. 3. The isotherms show an increase of the equilibrium hydrogen pressure and an increase in the amount of hydrogen observed for the nanocomposite Mg_2Ni/Pd material (curve a) in comparison with those in the nanocomposite $Mg_{1.5}Al_{0.5}Ni/Pd$ (curve b). It is well known that alloys exhibiting a lack of a well-formed but small rise of pressure on their absorption/desorption isotherms can be recognized as useful materials for negative electrodes in Ni-MH cells.

At room temperature, the original nanocrystalline Mg_2Ni alloy absorbs hydrogen, but almost does not desorb it. At temperatures above 250 °C the reaction with hydrogen is reversible and the kinetics of the absorption-desorption process improves considerably. The hydrogen content in this material at 300 °C is 3.25 wt.%. When hydrogen is absorbed by Mg_2Ni beyond 0.3 H per formula unit, the system undergoes a structural rearrangement to the stoichiometric complex Mg_2Ni-H

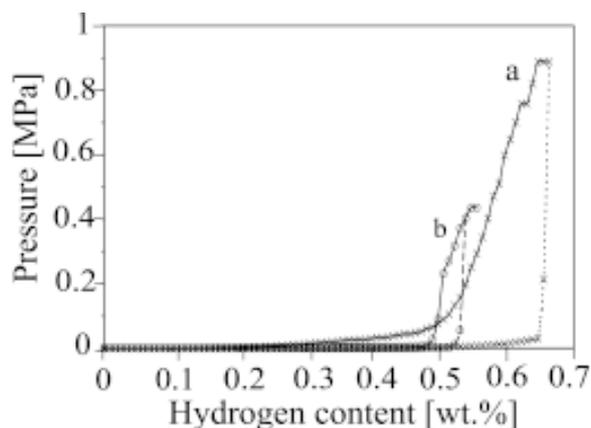


Fig. 3. Electrochemical pressure-composition isotherms for absorption (solid line) and desorption (dashed line) of hydrogen on nanocrystalline $\text{Mg}_2\text{Ni}/\text{Pd}$ (a), $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}/\text{Pd}$ (b) hydrogen storage materials; (6M KOH solution; the charge/discharge conditions were 4 mA g^{-1} and the cut-off potential was -0.700 V).

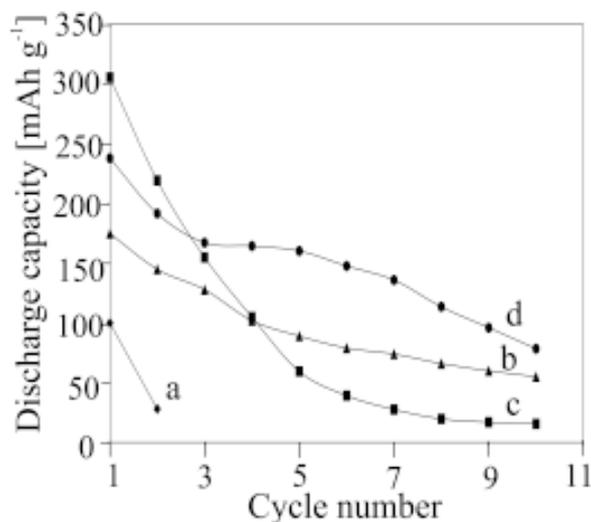


Fig. 4. Discharge capacities of nanocrystalline Mg_2Ni (a), $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ (b) and nanocomposite $\text{Mg}_2\text{Ni}/\text{Pd}$ (c), $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}/\text{Pd}$ (d) hydrogen storage materials; (current density of charge/discharge was 4 mA g^{-1}).

hydride, with an accompanying 32% increase in volume [12].

The Mg_2Ni electrode displayed the maximum discharge capacity (100 mA h g^{-1}) at the 1st cycle but degraded strongly with cycling (Fig. 4). The poor cyclic behaviour of Mg_2Ni electrodes is attributed to the formation of $\text{Mg}(\text{OH})_2$ on the electrodes, which has been considered to arise from the charge-discharge cycles [13]. The effect of magnesium substitution by Al in Mg_2Ni -type material, avoiding the surface oxidation, greatly improved the discharge capacities. In nanocrystalline $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ alloy discharge capacities up to 175 mA h g^{-1} was measured. The alloy containing Al was characterised by smoother surface than that of Al-free alloy [14]. Moreover aluminium formed an oxide coating of Al_2O_3 on the surface of the alloy and thereby improved the electrode performance.

Additionally, we have examined the effect of palladium coating on Mg_2Ni - and $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ -type materials (see Figs. 1b and 2b). Ball milling with palladium is responsible for a sizeable reduction of the crystallite sizes of Mg_2Ni - and $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ materials from 25 to 30 nm to 25 nm and 25 nm to 20 nm, respectively (Table 1).

The discharge capacity of coated nanocrystalline Mg_2Ni - and $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ -powders

with palladium was improved. The elemental Pd was distributed on the surface of ball milled alloy particles homogenously and role of these particles is to catalyse the dissociation of molecular hydrogen on the surface of studied alloy [13]. Mechanical coating with palladium effectively reduced the degradation rate of the studied electrode material. Compared to that of the uncoated powders, the degradation of the coated was suppressed (Fig. 4).

4. CONCLUSION

Nanocrystalline $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$ - and nanocomposite $\text{Mg}_{2-x}\text{Al}_x\text{Ni}/\text{Pd}$ -type hydrogen storage materials ($x=0, 0.5$) synthesized by mechanical alloying followed by annealing treatment were used as negative electrode materials for Ni-MH battery. The studies show, that electrochemical properties of Mg-based electrode materials are the function of chemical composition of the used electrode materials. In the nanocrystalline Mg_2Ni powder, discharge capacity up to 100 mA h g^{-1} was measured. It was found that aluminium substituting magnesium in $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$ alloy greatly improved the discharge capacity of studied material. In nanocrystalline $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Ni}$ powder, discharge capacities up to 175

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