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Electronic and electrochemical properties of Mg_2Ni alloy doped by Pd atoms*

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The structure and electrochemical properties of nanocrystalline Mg_2Ni and Mg_2Ni/Pd nanocomposite have been studied. The materials were prepared by mechanical alloying. In nanocrystalline Mg_2Ni powder, discharge capacities up to 100 $mA \cdot h \cdot g^{-1}$ were measured. It was found that mechanically coated Mg-based alloys with palladium have effectively reduced the degradation rate of the studied electrode materials. Finally, the properties of nanocrystalline alloys and their nanocomposites were compared to those of microcrystalline samples. The electronic structure was studied by *ab initio* calculations, which showed that the 3b positions in the unit cell are preferred by the Pd impurities.

Key words: *Mg-based alloy; Pd coating; nanocrystalline alloy; metal hydride; electronic structure*

1. Introduction

Magnesium-based alloys have been extensively studied during last years but the microcrystalline Mg_2Ni alloy can reversibly absorb and desorb hydrogen only at high temperatures [1, 2]. Substantial improvements in the hydriding-dehydriding properties of Mg-type metal hydrides could possibly be achieved by formation of nanocrystalline structures [3, 4]. Additionally, it was found that the electrochemical activity of nanocrystalline hydrogen storage alloys can be improved in many ways, by alloying with other elements, by ball-milling the alloy powders with a small amount of nickel or graphite powders [4–7]. In order to optimize the choice of the intermetallic compounds for a battery application, a better understanding of the role of each alloy con-

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stituent on the electronic properties of the material is crucial. The nanocrystalline metal hydrides offer a breakthrough in prospects for practical applications. Their excellent properties (significantly exceeding those of traditional hydrides) result from combined engineering of many factors: alloy composition, surface properties, microstructure, grain size and others.

We have synthesized nanocrystalline Mg_2Ni alloy and Mg_2Ni/Pd nanocomposite. The influence of microstructure on the structural, electrochemical and electronic properties of synthesized materials was studied.

2. Experimental and computational details

Nanocrystalline Mg-type alloys were prepared using mechanical alloying followed by annealing. The powders were examined by XRD analysis, using CoK_α radiation. Mechanically alloyed (MA) and annealed Mg_2Ni powder was mixed with 10 wt. % of palladium 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. Independently, the microcrystalline Mg_2Ni alloy was synthesized by diffusion method.

Table 1. Structure, lattice parameters and discharge capacities for nanocrystalline Mg_2Ni-type materials[a]

Material	Structure and lattice constants [Å]	Discharge capacity [mA·h/g]	
		1st cycle	3rd cycle
Nanocrystalline Mg_2Ni	hexagonal, a = 5.216, c = 13.246	100	5
Nanocomposite Mg_2Ni/Pd	hexagonal/cubic, a = 5.216, c = 13.246/a = 3.890	308	162
Microcrystalline Mg_2Ni	hexagonal, a = 5.223, c = 13.30	–	–

[a] Data for parent microcrystalline Mg_2Ni alloy were also included for comparison.

In order to study electronic structure of the Mg_2Ni and $Mg_2Ni_{0.9}Pd_{0.1}$ compounds the full-potential local-orbital (FPLO) method has been used [8, 9]. The scalar-relativistic mode was used in the calculations including coherent potential approximation (CPA) [10] to take into account chemical disorder introduced by Pd impurities. The calculations were carried out for the hexagonal Mg_2Ni-type structure with $P6_222$ space group and experimental values of the lattice constants (Table 1). For the calculations we assumed the following configurations of atoms: core + semi core (2s2p) + valence (3s3p3d) electrons for Mg atoms, core + semi core (3s3p) + valence (4s4p3d) electrons for Ni atoms, and core + semi core (4s4p) + valence (5s5p4d) electrons for Pd atoms. The calculations were performed for the reciprocal space mesh containing 252 (for doped systems) and 2310 (for Mg_2Ni) points within the irreducible wedge (1/12) of the Brillouin zone using the tetrahedron method [11] for integrations.

The exchange-correlation potential was assumed in the form proposed by Perdew and Wang [12]. The self consistent criterion was equal to 10^{-8} Ry for the total energy.

3. Results and discussion

The effect of MA processing was studied by X-ray diffraction and by electrochemical measurements. In the present work, nanocrystalline and microcrystalline Mg_2Ni alloy and Mg_2Ni/Pd nanocomposite have been prepared by MA method followed by annealing, by a diffusion method and by ball milling, respectively (Table 1).

3.1. Mg_2Ni-type alloys

Figure 1 shows a series of XRD spectra of mechanically alloyed 2Mg–Ni powder mixture (0.453 wt. % Mg + 0.547 wt. % Ni) subjected to milling in increasing time.

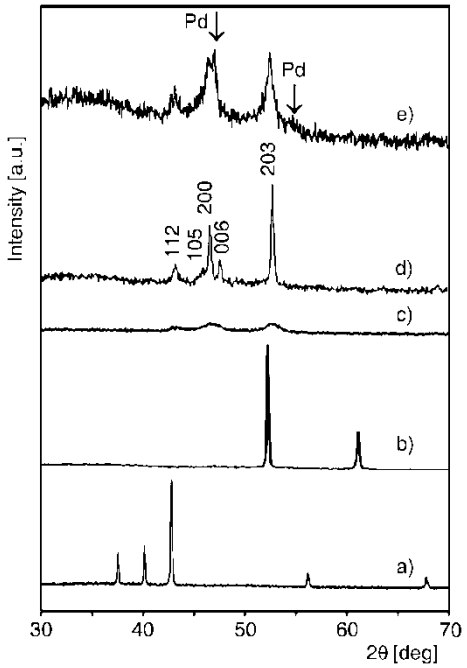

Fig. 1. X-ray diffraction patterns ($CoK_{\alpha 1}$) of pure powders of magnesium (a) and nickel (b) and mixture of 2Mg and Ni powders after MA for 45 h (c) followed by annealing at 723 K for 1 h (d); curve (e) represents XRD spectrum of Mg_2Ni/Pd composite prepared by MA for 1 h of nanocrystalline Mg_2Ni (see Fig. 1d) mixed with 10 wt. % Pd powder

The originally sharp diffraction lines of Mg and Ni (Fig. 1a) gradually become broader and their intensities decrease with milling time. The nanostructured Mg_2Ni with broad diffraction peaks are already found after 5 h of MA process. The powder mixture milled for more than 30 h has transformed directly to a hexagonal-type phase (Fig. 1b). Finally, the obtained powder was heat treated in high purity argon atmosphere at 450 ºC for 0.5 h to obtain the desired microstructure (Fig. 1c). Table 1 reports

the cell parameters of all the studied materials. The average size of amorphous 2Mg-Ni powders (AFM studies) was of the order of 30 nm.

At room temperature, original nanocrystalline alloy, Mg_2Ni, absorbs hydrogen but almost does not desorb it. At temperatures above 250 ºC, the kinetics of the absorption–desorption process improves considerably and for nanocrystalline Mg_2Ni alloy the reaction with hydrogen is reversible. The hydrogen content in this material at 300 ºC is 3.25 wt. %. Upon hydrogenation, Mg_2Ni transforms into the hydride Mg_2Ni–H phase [13].

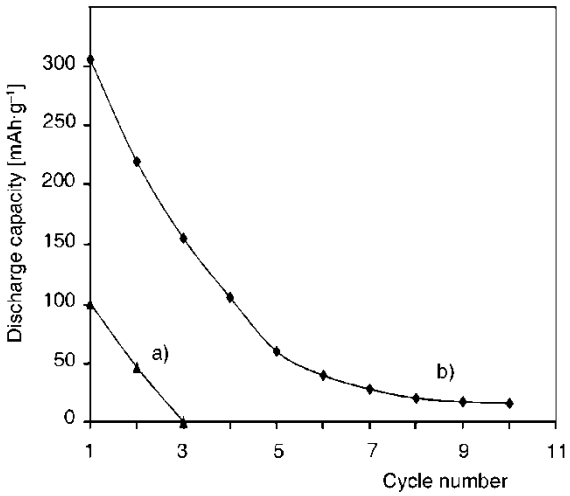

Fig. 2. Discharge capacity as a function of the cycle number for MA and annealed Mg_2Ni (a) and Mg_2Ni/Pd electrodes (b) (solution, 6 M KOH, 20 ºC)

The Mg_2Ni electrode, mechanically alloyed and annealed, displayed the maximum discharge capacity (100 $mA \cdot h \cdot g^{-1}$) at the first cycle but degraded strongly with cycling (Fig. 2). The poor cyclic behaviour of Mg_2Ni electrodes is attributed to the formation of $Mg(OH)_2$ on the electrodes which has been considered to arise from the charge -discharge cycles.

3.2. Effect of ball-milling with palladium

In order to improve the electrochemical properties of the studied nanocrystalline electrode materials, the ball-milling technique was applied to the Mg-based alloys using the palladium as surface modifiers (Fig. 1). Figure 2 and Table 1 show the discharge capacities as a function of the cycle number for studied nanocomposite material. The discharge capacity of nanocrystalline Mg_2Ni coated with palladium powder was increased. The elemental palladium 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. Mechanical coating with palla-

dium effectively reduced the degradation rate of the studied electrode materials. Compared to that of the uncoated powders, the degradation of the coated ones was suppressed. Recently, Iwakura et al. [14] have demonstrated that the modification of graphite on the MgNi alloy in the MgNi–graphite composite is mainly a surface one. Graphite inhibits the formation of new oxide layer on the surface of the material once the native oxide layer is broken during the ball-milling process.

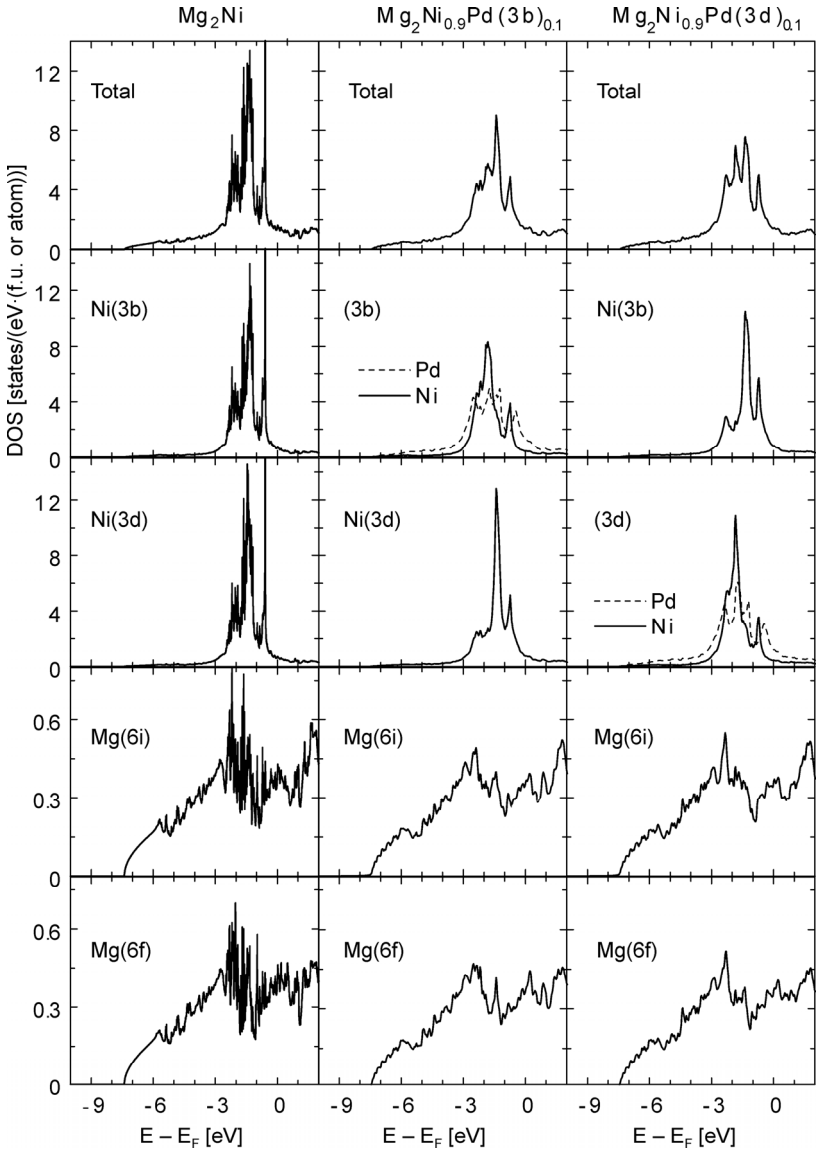

Fig. 3. Densities of states, total (per formula unit) and site projected (per atom) for Mg_2Ni and doped systems by Pd impurities located in 3b or 3d sites

The results of band structure calculations are presented in Fig. 3. We assumed that Pd impurities may replace only Ni atoms in 3b and 3d sites, the Mg sites do not accommodate Pd impurities. Figure 3 presents the DOS plots for the Mg_2Ni alloy and the doped systems $Mg_2Ni_{0.9}Pd_{0.1}$. The results for Mg_2Ni alloy are similar to those obtained earlier [15] using the LMTO method. Here, these results are treated as reference to monitor changes caused by the Pd impurities. We observe that the DOS plots for the doped systems are broadened, especially in sites occupied simultaneously by Pd and Ni atoms. The valence bands are dominated by Ni and Pd atoms because of large number of Ni(3d) and Pd(4d) electrons. The contribution provided by the Mg atoms is very small. The total energy calculations showed that 3b sites are preferred by the Pd impurities.

4. Conclusions

It was found that milling of 10 wt. % of palladium is sufficient to improve the discharge capacity of studied Mg-based nanocomposites. The experimental XPS valence bands measured for MA nanocrystalline alloys showed a significant broadening compared to those obtained for the microcrystalline samples with the same chemical composition. This is probably due to a strong deformation of the nanocrystals in the mechanically alloyed samples. The substitution of Mg in Mg_2Ni by transition metals leads to significant modifications of the shape and width of the valence band of the nanocrystalline as well as microcrystalline samples. Especially, the valence band shape of the MA nanocrystalline alloys is considerably modified compared to that measured for the microcrystalline samples. The strong modifications of the electronic structure in the MA nanocrystalline alloys could significantly influence their hydrogenation properties. The mechanical alloying is a suitable procedure for obtaining nanocrystalline Mg_2Ni-based alloy electrodes.

The *ab initio* band structure calculations showed that the valence bands are dominated by the Ni(3d) and Pd(4d) electrons, and the Pd impurities prefer 3b sites in the unit cell.

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