ELECTRONIC PROPERTIES OF NANOCRYSTALLINE Mg$_2$Ni-TYPE ALLOYS

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Abstract: Nanocrystalline Mg$_2$M$_x$Ni alloys (M = Mn, Al) were prepared by mechanical alloying followed by annealing. Formation of the nanocrystalline alloy was achieved by annealing of the amorphous material in high purity argon atmosphere at 723 K for 0.5 h. The experimental valence bands measured for mechanically alloyed nanocrystalline alloys showed a significant broadening compared to those obtained by theoretical band calculations. This is probably due to a strong deformation of the nanocrystals in the mechanically alloyed samples. The nanocrystalline Mg$_2$Ni electrode, displayed the maximum discharge capacity (100 mA h g$^{-1}$) at the 1st cycle but degraded strongly with cycling. In nanocrystalline Mg$_{1.5}$Mn$_{0.5}$Ni alloy discharge capacities up to 241 mA h g$^{-1}$ were measured.

1. INTRODUCTION

A large number of experimental investigation on LaNi$_5$, TiFe, ZrV$_2$-type compounds have been performed up to now in relation to their exceptional hydrogenation properties [1]. Magnesium-based hydrogen storage alloys have been also considered to be possible candidates for electrodes in Ni-MH batteries [2].

In order to optimise the choice of the intermetallic compounds for a selected application, a better understanding of the role of each alloy constituent on the electronic properties of the material is crucial. Several semi-empirical models [3, 4] have been proposed for the heat of formation and heat of solution of metal hydrides and attempts have been made to justify the maximum hydrogen absorption capacity of the metallic matrices. These models showed that the energy of the metal-hydrogen interaction depend both on geometric and electronic factors.

In this contribution, we study experimentally the electronic properties of nanocrystalline Mg$_2$Ni-type alloys using X-ray photoelectron spectroscopy (XPS). For a comparison, we will also show theoretical XPS valence bands calculated by LMTO method. These studies may supply useful indirect information about the influence of the electronic structure of nanocrystalline Mg$_2$Ni-type alloys on their hydrogenation properties.
2. EXPERIMENTAL PROCEDURE

The nanocrystalline Mg$_2$Ni-type alloys were prepared using mechanical alloying (MA) followed by annealing. MA was performed under argon atmosphere using a SPEX 8000 Mixer Mill. The purity of the starting metallic elements Mg, Ni, Al, and Mn was 99.9, 99.9, 99.95, 99+ wt.%, respectively. The mill was run up to 90 h for every powder preparation. The as-milled powders were heat treated at 723 K for 0.5 h under high purity argon to form an ordered phase. The MA process of the Mg$_2$Ni-type mixtures has been studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The change in the structure of powdered samples was observed using Atomic Force Microscope (AFM). The metal hydride syntheses were carried out in a high-pressure reactor chamber of a conventional Sieverts-type volumetric system.

The bulk chemical composition of the samples was measured under environmental conditions by X-ray fluorescence (XRF) method. The surface chemical composition and the cleanliness of the samples were measured in the ultra high vacuum (UHV) using XPS and Auger photoelectron spectroscopy (AES). Before loading to the UHV preparation chamber, the sample of the studied material with a well-polished surface was rinsed with twice-distilled water and dried in air. In the preparation chamber (10$^{-7}$ Pa) the sample was mounted on the holder equipped with a heater using a special transfer system. The sample was first heated in the preparation chamber (base pressure 10$^{-7}$ Pa) at 525 K for 3 h and then in-situ transferred to the analysis chamber (base pressure 4 × 10$^{-9}$ Pa) for the XPS measurements. The sample surface was cleaned here by ion (Ar$^+$, 3 kV) bombardment until the oxygen and carbon free well-defined surface of the sample with earlier selected chemical composition was obtained. The above UHV heating procedure at relatively low temperature does not change the microstructure of the studied samples. The XPS spectra were measured at room temperature (RT) using a SPECS EA 10 PLUS energy spectrometer with Al K$\alpha$ radiation of 1486.6 eV. The energy spectra of the electrons were analysed by a hemispherical analyser (FWHM$_{Mg\ K\alpha} = 0.8$ eV for Ag 3d$_{5/2}$).

The band structure calculations were performed based on TB LMTO method in the atomic sphere approximation (ASA) for ideal hexagonal Mg$_2$Ni type structure with P6$_3$22 space group. The theoretical photoemission spectra were obtained from calculated partial densities of states for the constituent atoms of the compound, multiplying them by a weight factor proportional to the atomic cross section for the photon scattering, given in the tables by Yeh and Lindau [5] and convoluting the products with the gaussian function to account for the finite experimental resolution.
3. RESULTS AND DISCUSSION

Figure 1a shows XRD pattern of an initial state (elemental powder mixture) of 2Mg and Ni powders (0.453 wt% Mg + 0.547 wt% Ni). The originally sharp diffraction lines of Mg and Ni (Fig. 1a) gradually become broader and their intensity decreases with milling time. The nanostructured Mg$_2$Ni with broad diffraction peaks are already found after 5 h of MA process. The powder mixture milled for more than 90 h has transformed completely to the amorphous phase, without formation of another phase (Fig. 1b). Formation of the nanocrystalline alloy was achieved by annealing the amorphous material in high purity argon atmosphere at 723 K for 0.5 h (Fig. 1c). All diffraction peaks were assigned to those of the hexagonal crystal structure with cell parameters $a = 5.216$ Å, $c = 13.246$ Å. The unit cell volume of nanocrystalline Mg$_{1.75}$M$_{0.25}$Ni (M = Al, Mn) system decreased with the increase in M contents. The atomic sizes of Mn and Al are smaller than that of Mg. For $x = 0.5$ in Mg$_{2}$M$_{x}$Ni system (Fig. 1c) the crystalline phase of a CsCl-type cubic structure is formed. The similar results were obtained earlier for (Mg$_{1-x}$Al$_x$)$_x$Ni system ($x = 0.2-0.5$) produced by MA by Orimo et al. [6, 7]. The average size of nanocrystalline grains, according to AFM studies, was of the order of 30 nm.

At room temperature, the original nanocrystalline alloy, Mg$_2$Ni, absorbs hydrogen, but almost does not desorb it. At temperatures above 523 K the kinetic of the absorption-desorption process improves considerably and for nanocrystalline Mg$_2$Ni alloy the reaction with hydrogen is reversible. The hydrogen content in this material at 573 K is 3.25 wt%. Upon hydrogenation, Mg$_2$Ni transforms into the hydride Mg$_2$Ni-H phase. It is important to note, that between 483-528 K the hydride Mg$_2$Ni-H phase transforms from a high temperature cubic structure to a low temperature monoclinic phase [8]. When hydrogen is absorbed by Mg$_2$Ni beyond 0.3 H per formula unit, the system undergoes a structural rearrangement to the stoichiometric complex Mg$_2$Ni-H hydride, with an accompanying 32% increase in volume.
The Mg\textsubscript{2}Ni electrode, mechanically alloyed and annealed, displayed the maximum discharge capacity (100 mA h g\textsuperscript{-1}) at the 1\textsuperscript{st} cycle but degraded strongly with cycling. The poor cyclic behaviour of Mg\textsubscript{2}Ni electrodes is attributed to the formation of Mg(OH)\textsubscript{2} on the electrodes, which has been considered to arise from the charge-discharge cycles [9]. To avoid the surface oxidation, we have examined the effect of magnesium substitution by Mn and Al in Mg\textsubscript{2}Ni-type material. This alloying greatly improved the discharge capacities. In nanocrystalline Mg\textsubscript{1.5}Mn\textsubscript{0.5}Ni alloy discharge capacities up to 241 mA h g\textsuperscript{-1} were measured.

The DOS and theoretical XPS plots for Mg\textsubscript{2}Ni and the systems doped by Al and Mn atoms are presented in Fig. 2. The band structure calculations were performed for ideal hexagonal Mg\textsubscript{2}Ni type structure with P6\textsubscript{3}2\textsubscript{2}2 space group. In this structure magnesium and nickel atoms each occupied two non-equivalent crystallographic positions: Mg(6i), Mg(6f), Ni(3d), and Ni(3b). Our total energy calculations showed that in both cases, Mg\textsubscript{11/6}Al\textsubscript{1/6}Ni and Mg\textsubscript{11/6}Mn\textsubscript{1/6}Ni, the substituted atoms, Al and Mn, prefer (6i) position. Results showed that Al atoms modify bottom of the valence band which is broader compared to that calculated for Mg\textsubscript{2}Ni system. In the case of Mn atoms, 4d electrons modify valence band in the range of 3 eV below the Fermi level (E\textsubscript{F}) and the value of DOS for E = E\textsubscript{F} is higher.

Results of our calculations should be treated as preliminary. As continuation of present calculations, we are going to perform them using the coherent potential approximation (CPA) to take into account chemical disorder in the doped Mg\textsubscript{2-x}(Al, Mn)\textsubscript{x}Ni systems. It is especially
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important for the systems with $x \geq 0.5$. For this concentration of impurities a structural transition is observed.

The experimental XPS valence bands measured for nanocrystalline Mg$_2$Ni and Mg$_{1.5}$Mn$_{0.5}$Ni are shown in Fig. 3. The experimental XPS valence bands measured for MA nanocrystalline alloys showed a significant broadening compared to those obtained by theoretical band calculations. Especially, a clear broadening of the band can be visible when compared experimental and theoretical XPS valence band for the Mg$_2$Ni alloy (see Fig. 3). Note, that the theoretical band calculation were performed for single-crystalline alloys. The substitution of Ni by Mn in the nanocrystalline Mg$_2$Ni alloy causes a further band broadening (Fig. 3). On the other hand, our XPS measurements showed that the substitution of Ni by Al leads only to a small valence band broadening (not shown in Fig. 3).

![Fig. 3. Experimental (solid lines) XPS valence band (Al-K$_\alpha$) spectra for nanocrystalline Mg$_2$Ni and Mg$_{1.5}$Mn$_{0.5}$Ni alloys. The XPS measurements were performed immediately after heating in UHV conditions followed by removing of a native oxide and possible impurities layer using ion gun etching system (see text). For a comparison we show theoretical XPS (broken line) of single-crystalline Mg$_2$Ni alloys (see Fig. 2).](image)

The reasons responsible for the band broadening of the nanocrystalline Mg$_2$Ni-type alloys are probably associated with a strong deformation of the nanocrystals in the MA samples [10]. Normally the interior of the nanocrystal is constrained and the distances between atoms located at the grain boundaries expanded [10]. Furthermore, the Al and Mn atoms could also occupied metastable positions in the nanocrystals. The strong modifications of the electronic structure of the nanocrystalline Mg$_2$Ni-type alloy could significantly influence on its hydrogenation properties [3, 4], similarly to the behaviour observed earlier for the nanocrystalline FeTi- [11] and LaNi$_5$-type [12] alloys.
4. CONCLUSIONS

The experimental XPS valence bands measured for MA nanocrystalline alloys showed a significant broadening compared to those obtained by theoretical band calculations. This is probably due to a strong deformation of the nanocrystals in the mechanically alloyed samples. The nanocrystalline Mg,Ni electrode, displayed the maximum discharge capacity (100 mA h g⁻¹) at the 1st cycle but degraded strongly with cycling. In nanocrystalline Mg₁.₃Mn₀.₇Ni alloy discharge capacities up to 241 mA h g⁻¹ were measured. 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 Mg,Ni-based alloy electrodes for Ni-MH batteries.

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References