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Surface segregation effect in nanocrystalline Mg–Ni alloys and composites

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X-ray photoelectron spectroscopy studies showed that the surface segregation of Mg atoms and width of the valence band in the nanocrystalline Mg_2Ni alloy are greater compared to those observed in polycrystalline Mg_2Ni thin films. Especially, a strong surface segregation of Mg atoms was observed for the Mg_2Ni/Pd composites. In this case, Mg atoms strongly segregate to the surface and form an Mg-based oxide layer under atmospheric conditions. The lower lying Ni and Pd atoms form a metallic subsurface layer and could be responsible for the observed, relatively high hydrogenation rate. Furthermore, the valence band broadening observed in the nanocrystalline Mg_2Ni alloys and Mg_2Ni/Pd composites could also significantly influence their hydrogenation properties.

Key words: *Ni–Mg alloy; nanocrystalline alloy; electronic structure*

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 also been considered to be possible candidates for electrodes in Ni-MH batteries [2].

An important process on the surface of the hydrogenated material is the splitting of hydrogen molecules into atoms. Many clean transition metal surfaces have the capability of dissociating hydrogen but lose this property upon oxidation. It is well known that the oxidation process causes the sealing of the surface to H_2 in metals and compounds such as Nb, V, Ta, FeTi, and others [3]. On the other hand, in a surface layer of $LaNi_5$, La segregates and Ni form ferromagnetic precipitations [3, 4]. Lantha-

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num atoms bind the impurities as oxide or hydroxide and keep the Ni metallic, which is then able to split the hydrogen molecule [3]. Therefore, the surface segregation process of lanthanum in the presence of O_2 or H_2O explained the excellent hydrogenation properties of $LaNi_5$ [3–5].

In this paper, we study the surface segregation effect in polycrystalline and nanocrystalline Mg_2Ni alloys and Mg_2Ni/Pd composites using X-ray photoelectron spectroscopy (XPS) with depth profile analysis. The structure of the samples has been studied by X-ray diffraction (XRD) with CoK_α radiation, and with an atomic force microscope (AFM). Their bulk chemical compositions were measured using the X-ray fluorescence (XRF) method. These studies may supply useful indirect information about the influence of the surface segregation effect in Mg–Ni-based alloys and composites on their hydrogenation properties.

2. Experimental procedure

Polycrystalline Mg–Ni alloy thin films were deposited onto glass substrates using a computer-controlled ultra high vacuum (UHV) magnetron co-sputtering. The chemical compositions and the cleanness of all layers were checked *in-situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-11} mbar) analysis chamber equipped with XPS. All emission spectra were measured immediately after transferring of the sample in a vacuum of 8×10^{-11} mbar. The thicknesses and compositions of the deposited films were determined using XRF.

The nanocrystalline Mg_2Ni-type alloys were prepared using mechanical alloying (MA), followed by annealing. MA was performed under argon atmosphere using a SPEX 8000 Mixer Mill. The purities of the starting metallic elements Mg and Ni were 99.9 and 99.95 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 1 h under high purity argon to form an ordered phase. Furthermore, we have also prepared Mg_2Ni/Pd composites with Pd content up to 10 wt. %. The MA and annealed Mg_2Ni powder were mixed with 10 wt. % Pd powder (74 μm, purity 99.95 %) and milled for 1 h in a SPEX Mixer Mill. The weight ratio of hard steel balls to mixed powder was 30:1.

The surface chemical compositions and the cleanness of the samples were measured in UHV using XPS and repeated 3 keV argon ion beam sputtering. Before loading to the UHV preparation chamber, a 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^{-9} mbar) 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 at 525 K for 3 h and then *in-situ* transferred to the analysis chamber for the XPS measurements. The above UHV heating procedure at relatively low temperature does not change the microstructure of the studied samples. The XPS spectra were recorded at room temperature using a SPECS EA 10 PLUS energy spectrometer with

AlK_α 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 $3d_{5/2}$).

3. Results and discussion

The MA process has been studied by XRD and microstructural investigations, using Mg_2Ni as a representative alloy example. Figures 1a and 1b show XRD patterns of the initial state (elemental powder mixture) of Mg and Ni powders, respectively. The originally sharp diffraction lines of Mg and Ni gradually become broader and their intensity decreases with milling time. Features due to nanostructured Mg_2Ni with broad diffraction peaks are already found after 5 h of MA process. XRD pattern of 2Mg and Ni powders (0.453 wt. % Mg + 0.547 wt. % Ni) after MA for 45 h is shown in Fig. 1c. The powder mixture milled for more than 45 h transform completely to the amorphous phase, without formation of another phase. Formation of the nanocrystalline alloy was achieved by annealing the amorphous material in high purity argon atmosphere at 723 K for 1 h (Fig. 1d). All diffraction peaks were assigned to those of the hexagonal crystal structure with cell parameters a = 5.216 Å, c = 13.246 Å. The

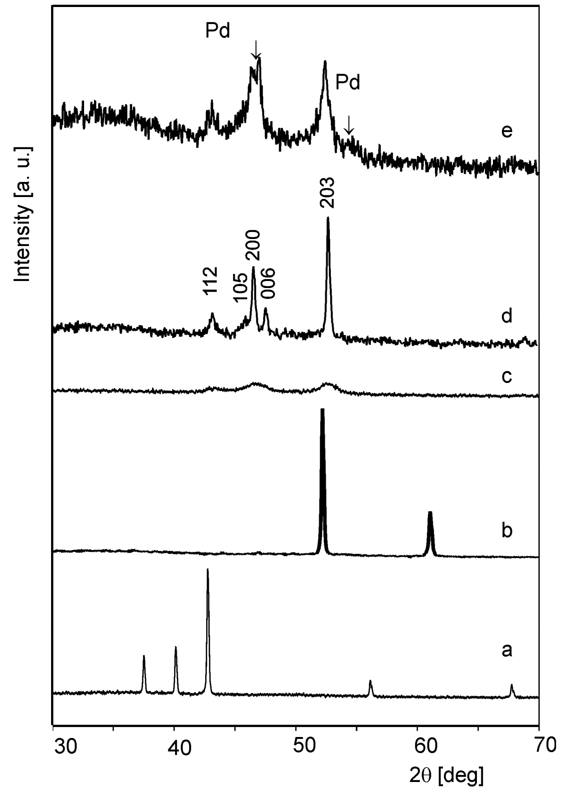

Fig. 1. X-ray diffraction patterns ($CoK_{\alpha 1}$) of pure powders of magnesium (a) and nickel (b), and a mixture of 2Mg and Ni powders after MA for 45 h (c) followed by annealing at 723 K for 1 h (d). Curve (e) represents XRD spectrum of Mg_2Ni/Pd composite

average size of nanocrystalline grains, according to AFM studies, was of the order of 30 nm. Curve e) in Fig. 1 represents XRD spectrum of the Mg_2Ni/Pd composite.

At room temperature, the original nanocrystalline alloy, Mg_2Ni, absorbs hydrogen but almost does not desorb it. At temperatures above 523 K, the kinetics of the absorption-desorption process improves considerably and for nanocrystalline Mg_2Ni alloy the reaction with hydrogen is reversible [6]. The hydrogen content in this material at 573 K is 3.25 wt. %. Upon hydrogenation, Mg_2Ni transforms into the hydride Mg_2Ni-H phase. It is important to note that between 483 and 528 K the hydride Mg_2Ni-H phase transforms from a high temperature cubic structure to a low temperature monoclinic phase [7]. When hydrogen is absorbed by Mg_2Ni beyond 0.3H per formula unit, the system undergoes a structural rearrangement to the stoichiometric complex Mg_2Ni-H hydride, with an accompanying 32% increase in volume.

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. 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 [8]. To avoid the surface oxidation, we have examined the effect of magnesium substitution by Mn and Al in Mg_2Ni-type material. This alloying greatly improved the discharge capacities. In the nanocrystalline $Mg_{1.5}Mn_{0.5}Ni$ alloy, discharge capacities up to 241 $mA\cdot h\cdot g^{-1}$ were measured [9].

The experimental XPS valence band measured for the MA nanocrystalline Mg_2Ni-type alloy and Mg_2Ni/Pd composite showed a significant broadening compared to that obtained for the polycrystalline thin film. The substitution of Ni by Mn in the nanocrystalline Mg_2Ni alloy causes a further band broadening [9]. The reasons for the band broadening of the nanocrystalline Mg_2Ni- type alloys and composites are probably associated with a strong deformation of the nanocrystals in the MA samples [10 -12]. The strong modifications of the electronic structure of the nanocrystalline Mg_2Ni-type alloy and composites could significantly influence its hydrogenation properties [13, 14], similarly to the behaviour observed earlier for the nanocrystalline FeTi- [11] and $LaNi_5$-type [12] alloys.

Results on XRF measurements revealed the assumed bulk chemical composition of the polycrystalline and nanocrystalline Mg_2Ni-type alloys. On the other hand, core -level XPS showed that the surface segregation of Mg atoms in the MA nanocrystalline samples is stronger compared to that of polycrystalline thin films. In particular, a strong surface segregation of Mg atoms was observed for the Mg_2Ni/Pd composites. Figure 2 shows normalised integral intensities of Mg, O, Ni, and Pd XPS peaks versus sputtering time as converted to the depth for Mg_2Ni/Pd composite. The XPS Mg 1s, Ni $2p_{3/2}$, and Pd $3d_{5/2}$ peaks were normalised to the intensities of in-situ prepared pure Mg, Ni, and Pd thin films, respectively. The oxygen 1s peak was normalised to the O 1s intensity in the MgO single crystal. Results presented in Fig. 2 show that Ni and Pd atoms are practically absent on the composite surface. On the other hand, Mg atoms strongly segregate to the surface and form a Mg based oxide layer under atmospheric conditions. The oxidation process is depth-limited so that an oxide-covering layer with a well-defined thickness is formed by which the lower lying metal is prevented from a further oxidation.

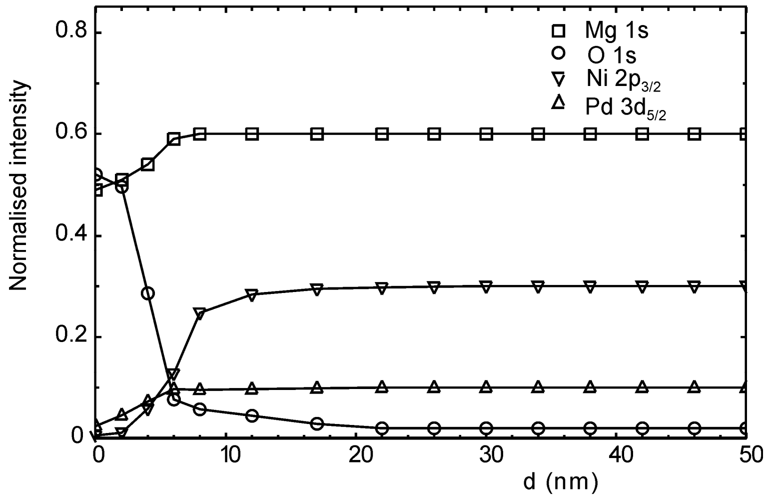

Fig. 2. Normalised integral intensities of Mg, O, Ni, and Pd XPS peaks versus sputtering time as converted to the depth for Mg_2Ni/Pd composite. The XPS Mg 1s, Ni $2p_{3/2}$, and Pd $3d_{5/2}$ peaks were normalised to the intensities of in-situ prepared pure Mg, Ni, and Pd thin films, respectively. The oxygen 1s peak was normalised to the O 1s intensity in the MgO single crystal. The XPS measurements were performed immediately after heating in UHV conditions (see text) which allowed us to remove the adsorbed impurities (mainly carbonates) excluding a stabile oxide top layer

In this way, one can obtain a self-stabilised oxide-metal structure. The lower lying Ni and Pd atoms form a metallic subsurface layer and are responsible for the observed relatively high hydrogenation rate [3, 4]. The surface segregation process of Mg atoms in Mg_2Ni/Pd composite is stronger compared to that observed for the Mg_2Ni nanocrystalline alloy. Furthermore, we have observed no segregation effect for the in-situ prepared polycrystalline Mg_2Ni thin films. On the other hand, the Mg_2Ni thin films naturally oxidised in air for 24 h show a small segregation effect of the Mg atoms to the surface.

4. Conclusions

The surface segregation process of Mg atoms in Mg_2Ni/Pd composite is stronger compared to that observed for the MA nanocrystalline Mg_2Ni alloy. Furthermore, the XPS valence bands measured in MA nanocrystalline alloys and composites showed a significant broadening compared to that obtained for polycrystalline thin film. Strong modifications of the electronic structure and surface segregation effect in the MA nanocrystalline alloys and composites could significantly influence their hydrogenation properties, similar to the behaviour observed earlier for the nanocrystalline FeTi-

[11] and $LaNi_5$-type [12] alloys. The mechanical alloying is a suitable procedure for obtaining Mg–Ni based alloy electrodes for Ni-MH batteries.

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