MICROENCAPSULATING $Mg_{1.8}Al_{0.2}Ni$ ALLOYS AND THEIR INFLUENCE ON PHYSICOCHEMICAL PROPERTIES

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Abstract

In this work, we have synthesised polycrystalline and nanocrystalline Mg_2Ni alloys by the combination of mechanical alloying and heat treatment at high or low temperatures. The influence of aluminium contents on the structural and electrochemical properties on Mg-based alloys will be presented. Additionally, to improve the electrochemical performance of studied alloys in alkaline solution, the effect of the nickel coating on the structure of the studied alloys and the electrodes characteristics were investigated. In Mg-based alloys coating with nickel effectively reduced the degradation rate of the studied electrode materials.

Introduction

With current storage materials it is not possible to excess a capacity of 2 wt.% H_2. Whereas for instance, magnesium can store 7 wt% H_2. Unfortunately MgH_2 is too stable and too much energy has to be expended in realising the hydrogen. Alloying magnesium with other elements could lower the stability of the hydride without reducing the capacity to an unacceptable value. For example, magnesium and nickel form stable Mg_2Ni compound. This alloy, which crystallizes in the hexagonal structure, is lighter and cheaper than the $LaNi_5$-type alloys. Upon hydrogenation, Mg_2Ni transforms into the hydride phase Mg_2NiH_4. The hydrogen content in Mg_2NiH_4 is also relatively high, being 3.6 wt%, whereas only 1.5 wt% in $LaNi_5H_6$.

In our work, we have synthesised polycrystalline and nanocrystalline Mg_2Ni and Mg-Ni alloys by the combination of mechanical alloying and heat treatment at high or low temperatures. The influence of aluminium contents on the structural and electrochemical properties on Mg-based alloys will be presented. Additionally, to improve the electrochemical performance of studied alloys in alkaline solution, the effect of the nickel coating on the structure of the studied alloys and the electrodes characteristics were investigated. In Mg-based alloys coating with nickel effectively reduced the degradation rate of the studied electrode materials.

Experimental

The Mg-based alloys of the following formulas: $Mg_{1.8}Al_{0.2}Ni$, were prepared by two different

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methods, by mechanical alloying method (MA) and by diffusion method (low-temperature synthesis in the solid state). The MA method described is in our earlier works [1, 2]. The method of the diffusion running to obtain of polycrystalline alloys consisted in mixing of substrates about the composition responding of the stoichiometry of the alloy in ball mill SPEX and to their warming by 24 h in the protective atmosphere of the argon at temperature 150 - 250°C. Then followed was second milling and second warming at the temperature 400°C. After finished heat-treatment of the sample one chilled to the room temperature. The MA and diffusion processes of the MgNi-type mixtures were studied by X-ray diffraction (XRD) using CoKα radiation, at various stages during milling and Atomic Force Microscope (AFM).

Before the preparation of metal hydride electrodes the powdered alloys were modified with thin and porous nickel coats. The microencapculation of the powdered alloys were carried out by electroless nickel plating process. The electroless nickel plating solution was made of $NiCl_2$ x 6 H_2O 30 g/l, CH_3COONa 10 g/l, and NaH_2PO_2 x H_2O 12 g/l, pH = 5.5 with HCl. A 100-ml reactor was water-jacket to keep the desired temperature within +/- 0.5 °C. The optimal working temperature was 60 °C. Before starting the process the surface of the alloy particles were activated by treatment with deionised water (60 °C) by 10 minutes with mechanical agitation; 1g of powder alloy per 25 ml of water. The well-prepared deposition solution (75 ml) was preheated to 60 °C and the pre-treated powdered alloy (25 ml of suspension of alloy) was added into the deposition solution. A mechanical agitation was applied to provide uniform distribution of powder in the reactor. After 10 minutes, the stirrer was stopped and the reacting solution was cooled to 20°C. The final steps were as following: (i) filtration and water washing, (ii) drying of powder in argon atmosphere.

Electrodes of hydrogen absorbing alloys were prepared by mixing the alloy powder modified or out with 10 wt.% addition of nickel powder. This powder mixture was pressed at 80 kN/cm^2 into ϕ 10.4 x 1.4 mm tablets. A pallet was then placed in a small basked of nickel gauze (current collector) and pressed again using a hand press. Before electrochemical testing the working electrodes composed of metal hydride electrode (MH) were chemically preactivation by treatments in 0.06M NH_4F solution. The experimental cell for electrochemical measurements consisted of the working electrode, the counter $Ni(OH)_2/NiOOH$ electrode made on sintered nickel carrier, the capacity of which many times exceeded that of the working electrode, and the reference Hg/HgO/6M KOH electrode. All potentials in this paper are reported vs. the latter electrode. The electrolyte was 6M KOH solution, and measurements were performed at room temperature. The constant current charge-discharge measurements were performed at current density i = 20 mA g^{-1} at room temperature. After one hour of a rest period for potential equilibration the electrode was discharged to the potential -0.7 V. A detailed description of the electrochemical measurements was given in Refs [1-3].

Electrochemical hydrogen absorption-desorption isotherms (electrochemical pressure-composition isotherms – EPC) were measured for the alloys above mentioned. The equilibrium pressure of hydrogen, $p(H_2)$, in hydride electrode, determined during the charge/discharge cycling, is the parameter allowing to predict the practical usefulness of alloy as negative electrode in Ni-MH cells.

EPC isotherms were recorded in the course of the periodic (0.5 h) charge/discharge cycles at a current density i = 20 mA g^{-1} of the alloy. After each cycle the electrodes were subjected to relaxation (0.5 h) at open circuit and then the measurements were continued.

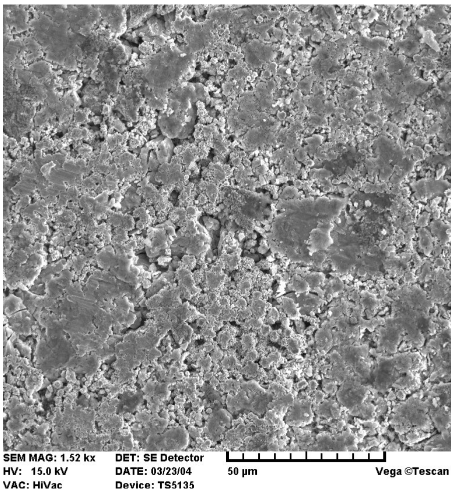
Results and discussion

In recent years, research and development of nickel hydride batteries using hydrogen storage alloys as a negative electrode material have been extensively conducted toward practical use; however, some difficulties still exist. It is well-known that hydrogen storage alloys, particularly powders, have very poor thermal conductivity and disintegrate into a very fine powder easily with the repeated cycling of hydrogen charging and discharging. It has been pointed out that the surface condition of alloy particles is one of the important factors affecting the characteristic of negative electrode.

The microencapsulation of the alloy powder with different kinds of electroless or galvanic coatings such as nickel or copper has been confirmed to be effective for improving the performance of negative electrode [4-6]. We think that this way of modification of hydrogen storage alloys may be a good solution to improve some new and promising alloys such as AB_2 type (Mg-Ni, Mg-Al-Ni), which are expected to offer a larger capacity, but are easily corroded in an electrolyte and thus causes serious deterioration during cycling.

In this work, an experimental study of physicochemical properties of $Mg_{1.8}Al_{0.2}Ni$ as hydrogen storage alloys is described, in which a main attempt was made to assess the effect Ni-encapsulation on them.

Electroless deposition of nickel is a well known technique for metallization of plastics and others nonconductors. This technique has the advantages of simplicity, low cost and the requirement of low annealing temperature. However, the plated surface must be a catalyst to the reaction in question; the best catalysts are Pd, Co and Ni. The common way to change inert surface, that will be plated, into active form (catalyst) is to cover it with catalyst by it treatment with an aqueous solution of $SnCl_2$ and HCl followed by treatment with an aqueous solution of $PdCl_2$ and HCl. The result of these treatment steps is generation of a huge number of micro islands of palladium particles that will be act as catalyst for reaction of nickel salt with sodium hypophosphine.



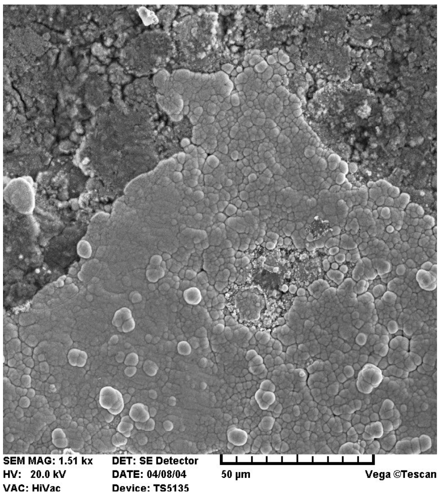


Fig. 1 *(left) Scaning electron micrograps of the base* $Mg_{1.8}Al_{0.2}Ni$ *alloy.*

Fig. 2 *(right) Scaning electron micrograps of the nickel coated* $Mg_{1.8}Al_{0.2}Ni$ *alloy.*

Scanning electron micrographs (SEM) of the surface of electrode produced from the $Mg_{1.8}Al_{0.2}Ni$ alloy is presented in Fig. 1. For comparing as can be seen in Fig. 2, the electrode executed from the same alloy, but with coated thin layer of the nickel. The surface of the bare alloy was smooth, but that the nickel-coated surface was protrude.

Balej [7] basing on the Nernst equation describes marking of isotherms of the absorption-desorption of hydrogen on equilibrium potential of the electrode, registered during periodic charging/discharging cycles with the solid current. The figure 3 introduces calculated on these dependences electrochemical isotherms of hydrogen absorption-desorption for the investigated alloys.

From comparison of the *EPC* curves for absorption-desorption (Fig.3), one can see that the nickel coated $Mg_{1.8}Al_{0.2}Ni$ alloy obtained by diffusion method demonstrate significantly higher concentration of hydrogen in practically preferred equilibrium pressure [8] as compared to the nickel coated $Mg_{1.8}Al_{0,2}Ni$ alloys obtained by MA method. It means that the former alloys offer good properties for application as negative electrode. The $Mg_{1.8}Al_{0.2}Ni$ alloys without nickel coating obtained by diffusion and MA method demonstrate properly lower concentration of hydrogen as compared to the alloys with nickel coating. Moreover, on *EPC* absorption-desorption curves for all samples of investigated alloys a wide hysteresis appears which indicates that only a part of hydrogen can be recovered during the discharged run of Ni-MH cell. It is worth noting that the conclusions arising from analysis of *EPC* curves (Fig. 3) are in a good consistency with those resulting from curves presented in Fig. 4.

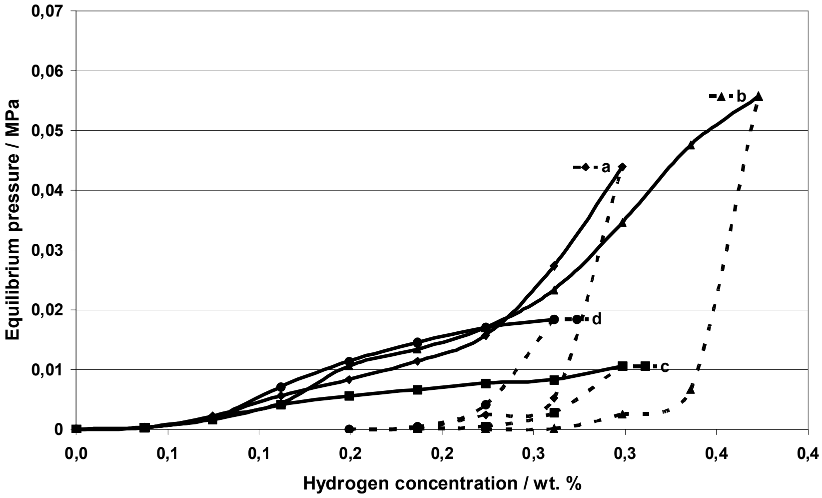


Fig. 3 *Electrochemical pressure-composition isotherm for absorption - desorption of hydrogen on* $Mg_{1.8}Al_{0.2}Ni$ *alloy at 293 K, prepared by: a- diffusion without nickel coating, b- diffusion with nickel coating, c- MA without nickel coating, d- MA with nickel coating.*

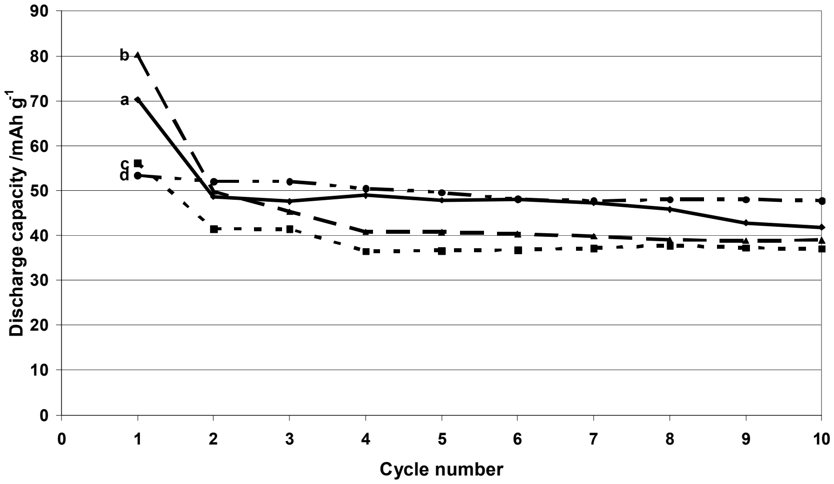


Fig. 4 *Discharge capacity as a function to the cycle number of the electrode from* $Mg_{1.8}Al_{0.2}Ni$ *alloy prepared by: a- diffusion without nickel coating, b- diffusion with nickel coating, c- MA without nickel coating, d- MA with nickel coating.*

The discharge capacities of negative electrode made of the bare and nickel-coated $Mg_{1.8}Al_{0.2}Ni$ alloy obtained by different methods were estimated in half cells and are plotted in Fig. 4 as a function of the cycle number. The highest capacity was found for the electrode made of the nickel-coated $Mg_{1.8}Al_{0.2}Ni$ alloy obtained by diffusion method. A distinctly lower discharge capacity was found for the nickel-coated $Mg_{1.8}Al_{0.2}Ni$ alloy obtained by mechanical alloying method. The increase in capacity for alloys with nickel coating obtained by diffusion and MA method in comparison to the alloys without nickel coating is parallel to the increase in the hydrogen concentration determined from both EPC isotherms (Fig.3).

The decrease in discharge capacity after the first ten charge/discharge cycles is dependent on their different solubility in KOH solution. The degradation of the bare alloys electrodes results from the degradation of surface properties by oxygen reaction in the alkaline solution. The degradation rate of the nickel-coated alloys is effectively reduced after the first ten charge/discharge cycles. Afterwards the alloys is disintegrated during the repeated charging /discharging process which brings about the gradual pulverisation of the alloy, continuously enlarged surface area, production of fresh surface resulting in continuous degradation of this alloys [9].

Conclusions

- ✓ The highest discharge capacity is observed for the electrodes produced by diffusion method and modified with thin and porous nickel coats;
- ✓ Initially the discharge capacity decreases but from the second cycle it remains constant;
- ✓ This decrease is the least for electrodes prepared by Mechanical alloying and modified with thin and porous nickel coats;
- ✓ The decrease discharge capacity is probably results from the degradation of alloys related to their pulverization, and, in the case of alloys with nickel coats to cracking of nickel layer.

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