ELECTROCHEMICAL BEHAVIOR OF POLYCRYSTALLINE AND NANOCRYSTALLINE AB_5 TYPE METAL HYDRIDES

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Abstract

The relations between electrochemical properties of polycrystalline and nanocrystalline [Mm(Al-Mn-Co-Ni)$_5$] alloys have been investigated. The polycrystalline alloys were prepared by arc melting under argon atmosphere, whereas the nanocrystalline alloys were synthesized by mechanical alloying and recrystallization by heat treatment in argon atmosphere. The structure of alloy powders was characterized by X-ray diffraction (*XRD*) analysis. To predict the electrochemical behaviour of the prepared alloys as negative electrodes for Ni-MH cells the electrochemical pressure-composition (*EPC*) isotherms were estimated from the rest potential of the alloy electrode. The electrochemical properties of polycrystalline and nanocrystalline alloys were characterized by the charge/discharge cycling in the half-cells and in the button cell.

Introduction

A proper selection of alloy elements and the preparation and activation methods of AB_5 alloys are principal conditions to obtain high discharge capacity, good durability and acting as catalyst in an electrode reaction. The intermetallic hydrogen storage compounds can be prepared by conventional methods, e.g., arc melting the stoichiometric amounts of the component elements in an arc or inductive furnace in an argon atmosphere [1-3]. Non – equilibrium processing, such as mechanical alloying (MA) can be utilized to synthesize highly activated nanocrystalline powders and has succeeded in synthesizing a wide range of electrode materials for rechargeable nickel – metal hydride batteries [4-8]. The starting materials for mechanical alloying are metal powders with a proper elemental composition. The MA process leads to an unstable alloy product, which form solid solution, intermetallic phase or amorphous material depending on thermodynamic conditions. During the MA process taking place in solid state, mechanically induced reactions proceed between components of alloy powders.

In this work electrochemical properties of polycrystalline and nanocrystalline [Mm(Al-Mn-Co-Ni)$_5$] alloys obtained by arc melting and MA were studied.

Experimental details

Two intermetallic hydrogen storage compounds differing in the distribution of the rare earth elements, of the following formulas: $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$, $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$, were prepared by two methods to obtain polycrystalline and nanocrystalline structure.

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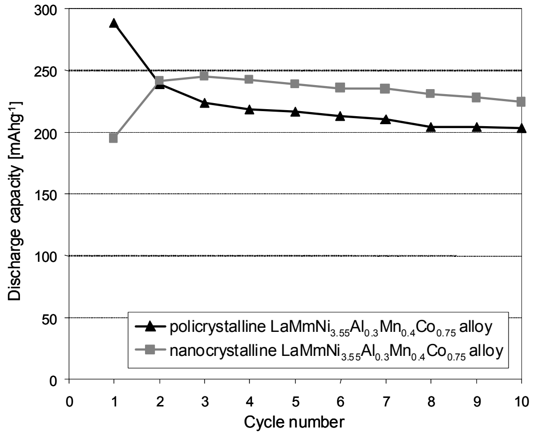
Polycrystalline alloys were prepared by arc melting in argon atmosphere using the mixture of La-mischmetal, Cs-mischmetal and pure metals (99.9% Merck) in proper atomic proportions. The casting was carried out in the Bühler arc furnace using a water-cooled copper crucible. The electrode material was produced by mechanical grinding in a hydraulic press followed by proper crushing to fine powder via cyclic hydrogen absorption/desorption from gaseous phase. As a consequence of this process polycrystalline [Mm(Al-Mn-Co-Ni)$_5$] (< 100 μm grain size) was obtained. After such a treatment the material was used for the preparation of working electrode.
The amorphous [Mm(Al-Mn-Co-Ni)$_5$] alloys were synthesized by the MA method using SPEX 8000 D Mill. The as-milled powders were heat treated at 1020 K for 0,5 h under high purity argon to form the hexagonal $CaCu_5$ phase. The nanocrystalline materials [Mm(Al-Mn-Co-Ni)$_5$] were obtained. This material served as the working electrode. Structural changes occurred in the alloy materials obtained by the mentioned methods were determined by X-ray diffraction analysis using CuK_α radiation.
The working electrodes of $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$, $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys obtained by arc melting and MA were prepared by mixing the alloy powder with 10 wt.% addition of nickel powder. This powder mixture was pressed into Ø10.4 x 1.4 mm tablets. A tablet was then placed in a small basket made of nickel gauze (current collector) and pressed again using a hand press. Before electrochemical testing the working electrodes were activated by chemical treatment in 12 M KOH solution [1]. 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. 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 = 40 mA g^{-1}. During the cycles the charge process was conducted till the beginning of the hydrogen evolution on electrode. After one hour of a rest period for potential equilibration the electrode was discharged to the potential -0.7 V.
Electrochemical hydrogen absorption/desorption isotherms (electrochemical pressure-composition isotherms – *EPC*) were measured above mentioned for the alloys. 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 the 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 current density i = 40 mAg^{-1} of alloy. After each cycle electrodes were subjected to relaxation (0.5 h) at open circuit and then the measurements were continued. The relation between the hydrogen equilibrium pressure and the amount of hydrogen absorbed in alloy electrodes was determined on the basis of the Nernst equation [9].

Results and discussion

The discharge capacities of negative electrodes made of the $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys obtained by different methods were estimated in half-cells and are plotted in Figs. 1-2 as a function of the cycle number. The electrodes are compared from the point of view of capacity and durability (Fig. 1-2). For the first cycle the highest capacity was found for the electrodes made of $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys obtained by arc melting (290 mAhg^{-1} and 260 mAhg^{-1}, respectively). Distinctly lower discharge capacities about 195 mAhg^{-1} and 250 mAhg^{-1}, respectively were found for the some alloys prepared by MA methods. It is interesting that the alloy prepared by MA method exhibits a gradually increasing discharge capacity during ten charge/discharge cycles, whereas the alloys of the same composition but obtained by both arc melting exhibit a gradually descending tendency. The decrease in discharge capacity after the first ten charge/discharge cycles might be ascribed to their different solubility in KOH solution and degradation of surface properties by oxygen penetration as well as the dissolution of elements in the electrolyte [10].



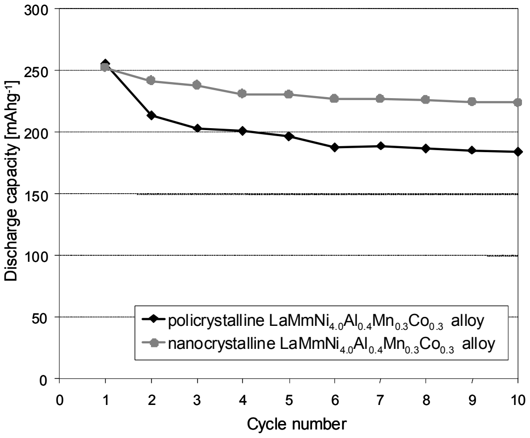
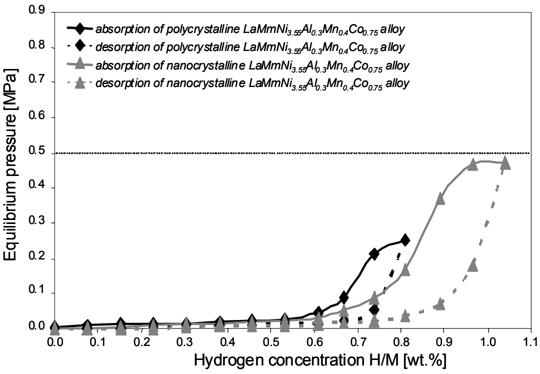


Fig. 1 *(left) Discharge capacity as a function of cycle number of the electrode made of polycrystalline and nanocrystalline* $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ *alloys*

Fig. 2 *(right) Discharge capacity as a function of cycle number of the electrode made of polycrystalline and nanocrystalline* $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ *alloys*

Distinction between discharge capacity of alloys obtained by arc melting and alloys obtained by MA is parallel to a difference in the hydrogen concentration determined from both EPC isotherms (Fig. 3-4).



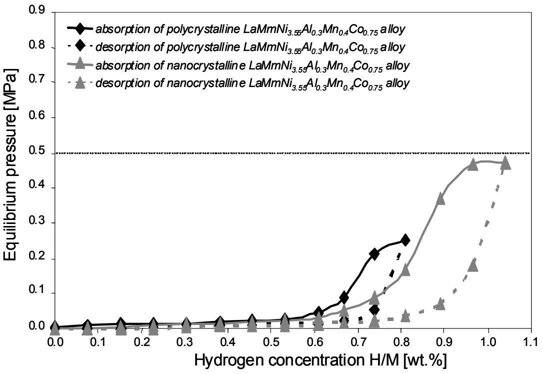


Fig. 3 *Electrochemical pressure-composition isotherms for absorption/desorption of hydrogen on polycrystalline and nanocrystalline* $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ *alloys determined at 293 K*

Fig. 4 *Electrochemical pressure-composition isotherms for absorption/desorption of hydrogen on polycrystalline and nanocrystalline* $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ *alloys determined at 293 K*

The *EPC* isotherms determined for the studied materials (polycrystalline and nanocrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys) are illustrated in Fig. 3-4.

In the present paper the capacity of alloy electrode in relation to the amount of absorbed hydrogen (wt.%) was calculated based on the put in/put out charge. In accordance with the above equation, the change of one order of magnitude in hydrogen pressure in alloy results in the change in electrode potential of 29 mV. It is well known that the alloys absorbing large amounts of hydrogen in the pressure range from 0.001 to 0.5 MPa are considered as suitable materials for MH electrodes [11].

From the comparison of *EPC* curves of absorption/desorption determined for polycrystalline and nanocrystalline alloys (Figs. 3-4), one can see that nanocrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys demonstrate significantly higher concentration of hydrogen as compared to polycrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys. However the nanocrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys require distinctly higher pressure for sorption of hydrogen (for nanocrystalline $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloy higher up 0.5 MPa). Moreover, on *EPC* absorption-desorption curves for sample of a nanocrystalline $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloy a wide hysteresis appears which indicates that only a part of hydrogen can be recovered during the discharge run of Ni-MH cell.

For the above reasons polycrystalline and nanocrystalline alloys of the following formulas $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ and $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ were then subjected to the cyclic life tests in the button cells. The cyclic behaviour of the alloys anodes were examined in the button HB 116/054 cell (according to the International Standard IEC No. 61952-2 related to the hydride button rechargeable single cell). The changes in discharge capacity upon test cycling are depicted in Fig. 5. As can see from Fig.5, the samples of polycrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$, $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys used as negative electrode in the button cell exhibit the same nominal value of discharge capacity (about 56 mAh), whereas the samples of nanocrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy exhibit lower capacity (about 52 mAh). In the button cell witch nanocrystalline $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloy used as negative electrode was observed unseal of button cell in consequence of considerable increase gas pressure during second cycle of charging.

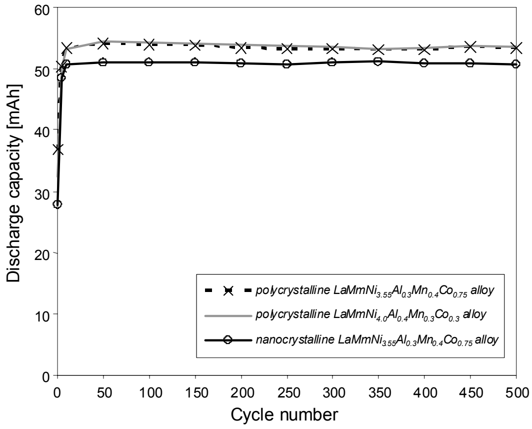


***Fig. 5** Durability of the button cell with negative electrode made of investigated alloys*

It is worth noting that the conclusions arising from analysis of *EPC* curves (Fig. 3-4) are in a good consistency with those resulting from durability curves presented in Fig. 5.

Conclusion

The studies demonstrate that the preparation methods of investigated alloys greatly influence their electrochemical capacities. Therefore there is a correlation between structural parameters and electrochemical characteristics for the examined alloys.
The nanocrystalline alloys tested in half-cells exhibit higher capacity in comparison to the polycrystalline alloys. The increase in capacity for these alloys is parallel to the increase in the hydrogen concentration determined from both *EPC* isotherms. However, distinctly higher pressure for sorption of hydrogen results in bad properties from the point of view of their application in Ni-MH batteries. Whereas the nickel metal-hydride button cells with polycrystalline $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$, $LaMmNi_{4.0}Al_{0.4}Mn_{0.3}Co_{0.3}$ alloys used as negative electrode can be successfully employed for producing commercial-batteries.

Acknowledgements

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