AMORPHOUS MG-NI-M-TYPE ALLOYS AS A HYDROGEN SOURCE IN FUEL CELLS

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Abstract

The amorphous Mg-Ni-M-type (M=AI, Mn, Ti, Zr) alloys have been synthesized by mechanical alloying (MA). The powder mixture milled for more than 70 h has transformed completely to the amorphous phase. The mechanically alloyed materials, with 10 wt. % addition of Ni powder, were subjected to electrochemical measurements as working electrodes. The discharge capacity of electrodes prepared by application of MA MgNi alloy powders was low. It was found that the partial substitution of magnesium by Mn, AI, Ti and Zr in MgNi alloy leads to an increase in discharge capacities.

Introduction

As a typical metal-hydrogen hydride system, magnesium and magnesium-based alloys were proposed as hydrogen storage materials [1-3]. Pure Mg can store 7 wt. % H₂, is abundant and available at low cost. Unfortunately MgH₂ 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, the polycrystalline Mg₂Ni alloy can reversibly absorb and desorb hydrogen only at high temperatures. Upon hydrogenation at 250 °C, Mg₂Ni transforms into the hydride phase Mg₂NiH₄ [1]. The hydrogen content in Mg₂NiH₄ is also relatively high, being 3.6 wt. %.

Substantial improvements in the hydriding-dehydriding properties of Mg-based alloys could possibly be achieved by formation of nanoscale structures [2-5]. Mechanical alloying is one of the approaches to produce Mg-Ni alloys which have been highly expected to be used as hydrogen storage materials [2]. Aoki et al. [6] pointed out that ball milling which gives rise to the creation of fresh surfaces and cracks is highly effective for the kinetic improvement in initial hydriding properties. Zaluski et al. [2] successfully prepared nanocrystalline Mg₂Ni to improve the hydriding properties of Mg₂Ni. In nanocrystalline Mg-Ni system the total hydrogen content increases with increasing Ni content [4]. Generally, it was found that the electrochemical activity of Mg-based hydrogen storage alloys at room temperature can be improved in many ways, by forming the non-stoichiometric structures [7], by alloying with other elements [8, 9]. For example, Lei et al. [9] have reported that a MgNi alloy prepared by mechanical alloying can charge and discharge at room temperature. On the other hand, Ye and co-workers [10] found that that manganese in amorphous Mg_{0.9}M_{0.1}Ni partially substituted by Ni, Ti, Co and Si could lead to the

Corresponding author: W. Majchrzycki Fax: +48-61-8793012, E-mail: majchrzycki@claio.poznan.pl improvement of hybriding/dehybriding properties, cyclic stability and discharge capacity. In this present work, the formation of amorphous MgNi, $Mg_{0.75}AI_{0.25}Ni$, $Mg_{0.75}Mn_{0.25}Ni$, $Mg_{0.90}Ti_{0.10}Ni$ and $Mg_{0.90}Zr_{0.10}Ni$ alloy powders prepared by mechanical alloying has been investigated. The electrochemical properties of this type of materials have been studied at room temperature.

Experimental

Mechanical alloying was performed under an argon atmosphere using a SPEX 8000 Mixer Mill (USA). The stainless steel vial was used. The composition of the starting powder mixture corresponded to the stoichiometry of the "ideal" reactions. The elemental powders (Mg: \leq 300 µm; Ni: 3–7 µm; Al: \leq 75 µm, Mn: \leq 45 µm; Ti: 45 µm; Zr: 150 µm) were mixed in the glove box (Labmaster 130) and poured into the vial. The mill was run up to 70 h for every powder preparation. The MA process of the MgNi-type mixtures has been studied by X-ray diffraction (XRD) using Co K α radiation, at various stages during milling and Atomic Force Microscope (AFM).

The mechanically alloyed hydrogen storage material with 10 wt. % of addition of nickel powder, were subjected to electrochemical measurements as working electrodes after pressing at 80 kN.cm⁻² to 0.3 g pellet form between basket made of nickel gauze (as a current collector). Before electrochemical testing the working electrodes were chemically activated in 0.06M NH_4F solution at 100 °C for 1 h. A detailed description of the electrochemical measurements was given in Refs. [11,12].

Results and discussion

The behaviour of MA process has been studied by X-ray diffraction and by AFM measurements Figure 1 shows a series of XRD spectra of mechanically alloyed Mg-Ni powder mixture subjected to milling in increasing time. The originally sharp diffraction lines of Mg and Ni (Fig. 1a) gradually become broader and their intensity decreases with milling time. The nanostructured MgNi with broad diffraction peaks are already found after 20 h of MA process. The powder mixture milled for more than 70 h has transformed completely to the amorphous phase, without formation of an other phases (Fig. 1c). The average size of amorphous Mg-Ni powders, according to AFM studies, was of the order of 30 nm.



Fig. 1 XRD spectra of a mixture of Mg and Ni powders mechanically alloyed for different times in an argon atmosphere: a) initial state (elemental powder mixture), b) after MA for 20 h and c) after MA for 70 h

Etching of electrodes in 0.06M NH₄F solution for 1h at 100 $^{\circ}$ C was sufficient for the initial activation. The MgNi electrode, mechanically alloyed, displayed the maximum discharge capacity (119 mA.h.g⁻¹) at the 1st cycle but degraded strongly with cycling (Fig. 2). The poor cyclic behaviour of MgNi electrodes is attributed to the formation of Mg(OH)₂ on the electrodes, which has been considered to arise from the charge-discharge cycles [13]. To avoid the surface oxidation, we have examined the effect of magnesium substitution by Al, Mn, Ti and Zr in MgNi-type material. This alloying greatly improved the discharge capacities (Table 1). For example, in amorphous Mg_{0.75}Mn_{0.25}Ni alloy discharge capacities up to 135 mA.h.g⁻¹ was measured. A similar phenomenon to that described here has been observed by Ye et al. in amorphous Mg_{0.9}M_{0.1}Ni-type powders (M=Ni, Ti, Zr, Co and Si) [10].



Fig. 2 Discharge capacities as a function of cycle number of studied amorphous materials prepared by MA: (a) MgNi; (b) $Mg_{0.75}AI_{0.25}Ni$; (c) $Mg_{0.75}Mn_{0.25}Ni$; (d) $Mg_{0.90}Ti_{0.10}Ni$ and (e) $Mg_{0.90}Zr_{0.10}Ni$ at current density of i= 40 mA.g⁻¹

The surface chemical composition of nanocrystalline Mg_2Ni -type alloy studied by X-ray photoelectron spectroscopy (XPS) showed the strong surface segregation under UHV conditions of Mg atoms in the MA nanocrystalline Mg_2Ni alloy [14]. This phenomenon could considerably influence the hydrogenation process in such a type of materials, too. The same surface segregation was observed earlier by Stefanov in Mg-Ni films, where magnesium was found to segregate at the surface [15].

Table 1 Discharge capacities of studied materials prepared by mechanical alloying (current density of charging/discharging was 40 mA.g⁻¹).

Alloy	Discharge capacity (mAh.g ⁻¹)
MgNi	118.75
Mg _{0.75} Al _{0.25} Ni	131.33
Mg _{0.75} Mn _{0.25} Ni	135.22
Mg _{0.9} Ti ₀₁ Ni	131.63
Mg _{0.9} Zr _{0.1} Ni	106.74

Conclusions

An amorphous Mg_{1-x}M_xNi (M=AI, Mn, Ti and Zr) alloys synthesized by mechanical alloying and annealing were used as negative electrode materials for Ni-MH_x battery. The amorphous phase forms directly from the starting mixture of the elements. The discharge capacity of electrodes prepared by application of MA MgNi alloy powders displayed low capacity (119 mA.h.g⁻¹). It was found that the partial substitution of magnesium by AI, Mn, Ti or Zr in MgNi alloy leads to an increase in discharge capacities. The results obtained in this study suggest that the hydriding properties of the Mg-based materials will be improved by the application of nanoscale structures.

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