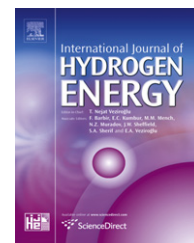


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Electrochemical hydrogen storage performance of Mg–Ti–Zr–Ni alloys

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ABSTRACT

Mg_{1.5}Ti_{0.5-x}Zr_xNi ($x = 0, 0.1, 0.2, 0.3, 0.4$), Mg_{1.5}Ti_{0.3}Zr_{0.1}Pd_{0.1}Ni and Mg_{1.5}Ti_{0.3}Zr_{0.1}Co_{0.1}Ni alloys were synthesized by mechanical alloying and their electrochemical hydrogen storage characteristics were investigated. X-ray diffraction studies showed that all the replacement elements (Ti, Zr, Pd and Co) perfectly dissolved in the amorphous phase and Zr facilitated the amorphization of the alloys. When the Zr/Ti ratio was kept at 1/4 (Mg_{1.5}Ti_{0.4}Zr_{0.1}Ni alloy), the initial discharge capacity of the alloy increased slightly at all the ball milling durations. The further increase in the Zr/Ti ratio resulted in reduction in the initial discharge capacity of the alloys. The presence of Zr in the Ti-including Mg-based alloys improved the cyclic stability of the alloys. This action of Zr was attributed to the less stable and more porous characteristics of the barrier hydroxide layer in the presence of Zr due to the selective dissolution of the disseminated Zr-oxides throughout the hydroxide layer on the alloy surface. Unlike Co, the addition of Pd into the Mg–Ti–Zr–Ni type alloy improved the alloy performance significantly. The positive contribution of Pd was assumed to arise from the facilitated hydrogen diffusion on the electrode surface in the presence of Pd. As the Zr/Ti atomic ratio increased, the charge transfer resistance of the alloy decreased at all the depths of discharges. Co and Pd were observed to increase the charge transfer resistance of the Mg–Ti–Zr–Ni alloys slightly.

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1. Introduction

Hydrogen is considered as an ideal fuel for many energy converters for the future. Great effort has been spent to find safe, effective and cheap method to store hydrogen. Among the various methods the storage in a solid state (in the form of metallic hydrides) has attracted great attention [1–4]. As compared to the conventional solid state hydrogen storage method (metallic phase and hydrogen gaseous reaction usually at elevated temperatures and high pressures), the electrochemical hydrogen storage method is more convenient for many applications [5,6]. Electrochemical hydriding does not need any gaseous hydrogen to store and does not require

high pressure and temperature. Instead, the atomic hydrogen directly enters into the metallic phase through electrochemical decomposition of water molecule at atmospheric pressure and room temperature (or moderate temperature). The main drawback of the electrochemical hydrogen storage, however, is the degradation of the metallic phase in highly basic aqueous medium.

Magnesium-based alloys have been studied extensively in the recent years the motivation being the utilization of these alloys as the negative electrode in nickel/metal hydride (Ni–MH) secondary batteries [7–14]. The common method for the synthesis of the Mg-based hydrogen storage alloys is the mechanical alloying [10,11]. Mechanical alloying provides

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easy and controlled synthesis of nanocrystalline or amorphous phases.

The main concern in the electrochemical hydrogen storage in Mg-alloys is the rapid degradation of the alloy storage capacity [7–13]. The hydroxide layer forms on the Mg-alloy surface during the hydriding/dehydriding cycles in alkaline solutions and retards the hydrogen in and out diffusion. The stability of this barrier hydroxide layer can be decreased by the partial replacements of Mg by various alloying elements [15]. Among the alloying elements zirconium [16–19], aluminum [20–23] and titanium [24–27] are considered as the most useful replacement elements for Mg. Recently we have reported the combined effects of Zr and Al replacement elements on the electrochemical hydrogen storage characteristics of Mg₂Ni phase by synthesizing (by the mechanical alloying) Mg_{1.5}Al_{0.5–x}Zr_xNi ($x=0, 0.1, 0.2, 0.3, 0.4, 0.5$) type alloys [28,29]. We found that Zr accelerated and Al decelerated the amorphization of Mg₂Ni phase [28]. Therefore Zr increased and Al decreased the alloy initial discharge capacity [28]. Aluminum was observed to improve the cyclic stability of Mg₂Ni phase considerably since the selective dissolution of the disseminated Al-oxide throughout the hydroxide layer destabilized the barrier layer [28].

In this work by keeping the Mg/Ni atomic ratio constant, the Zr/Ti atomic ratio was changed stepwise, and Mg_{1.5}Ti_{0.5–x}Zr_xNi ($x=0, 0.1, 0.2, 0.3, 0.4$) type alloys were synthesized by mechanical alloying in order to investigate the combined effect of Ti and Zr on the electrochemical hydrogen storage characteristics of Mg₂Ni phase. In addition to Mg–Ti–Zr–Ni quaternary alloys, Mg_{1.5}Ti_{0.3}Zr_{0.1}Pd_{0.1}Ni and Mg_{1.5}Ti_{0.3}Zr_{0.1}Co_{0.1}Ni alloys were also synthesized and the effects of Pd and Co on the alloy performance were observed.

2. Materials and methods

Elemental Mg, Ni, Ti, Zr, Pd and Co powders (325 mesh powders with at least 99.9% purity were obtained from Alfa Aesar) were mixed in various compositions and charged into the stainless steel vials under the high purity Ar atmosphere (in the glove box). The diameter of the stainless steel balls was 5 mm and the ball to powder weight ratio was selected as 20:1. The mechanical alloying was performed with a planetary ball mill (Fritsch, Pulverisette P-7) and the milling speed was 500 rpm. The ball milling duration was changed from 30 to 60 h. The mechanical alloying was carried out by milling for 30 min in the forward direction then cooling for 15 min and then milling for 30 min in the reverse direction. By this procedure the increase in the temperature of the vial was prevented and the better homogeneity was obtained. The vials, which have the special lids, were vacuumed and the high purity Ar gas was recharged into them at every 10 h during the ball milling to prevent the possible oxidation of the alloy powders.

The phase structure of the alloy powders was examined by the X-ray diffractometer (Bruker axs D8) using Cu K α radiation. The powder morphologies were observed by ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM).

Working electrodes were prepared by mixing 0.2 g alloy powder with 0.6 g nickel powder and then cold pressing into pellets of 10 mm in diameter, under a pressure of 10 ton cm⁻².

NiOOH/Ni(OH)₂ counter electrode and a Hg/HgO reference electrode were used to set up a three-electrode cell in 6 M KOH solution. Tests were performed with PARSTAT Model 2273 potentiostat/galvanostat unit. The charge current density was 100 mA g⁻¹ and the charging was carried out down to the severe gassing potential. The discharge current density was 25 mA g⁻¹ and the discharge cut-off potential was $-0.6 V_{\text{Hg/HgO}}$. The excitation voltage was 10 mV (peak to peak) and the applied frequency varied from 100 kHz to 0.01 Hz in the electrochemical impedance measurements. Before the impedance measurements the electrode was kept at the working potential for at least 1 h.

3. Experimental results and discussion

3.1. The structural and morphological characteristics of Mg_{1.5}Ti_{0.5–x}Zr_xNi alloys

The effect of stepwise change in the Zr/Ti atomic ratio, while keeping the Mg/Ni atomic ratio constant, on the structure of the 60 h milled alloys is shown in the overlaid XRD patterns in Fig. 1. All the alloys give almost the same pattern with a broad peak around 41.5° which can be assigned to amorphous structure. As the Zr content of the alloy increases the height of the broad peak decreases slightly in Fig. 1. This trend suggests that Zr with a bigger atomic size facilitates the amorphization of the alloy [28].

Scanning electron micrographs of Mg_{1.5}Ti_{0.5}Ni, Mg_{1.5}Ti_{0.3}Zr_{0.2}Ni and Mg_{1.5}Ti_{0.1}Zr_{0.4}Ni alloys synthesized by 60 h milling are given in Fig. 2, a, b and c, respectively. The fragmentation of the coarse, cold-welded particles into the fine powders in these figures shows the typical morphology of the amorphous-like alloys [28]. The grain size of the disintegrated particles varies between 0.7 μ and 1.0 μ .

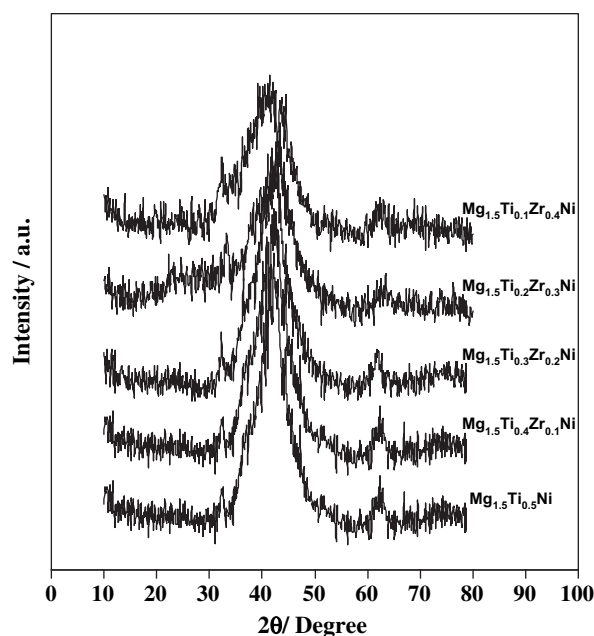


Fig. 1 – Overlaid XRD patterns of Mg_{1.5}Ti_{0.5–x}Zr_xNi ($x=0, 0.1, 0.2, 0.3, 0.4$) type alloys synthesized by 60 h milling.

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