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Synthesis and Electrochemical Properties of Mg-Ni-Y-Al Alloy with Mechanical Alloying

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Abstract. A powder material of Mg-Ni-Y-Al was synthesized by mechanical alloying method. Considerable amounts of amorphous and microcrystalline phases were formed after a mixture of elemental powder with the overall composition of $Mg_{67}Ni_{15}Y_9Al_9$ was mechanical alloyed for more than 80 hours. The phase formed in the synthesized powder material was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The electrochemical properties were examined with a solution of KOH.

Introduction

Magnesium-based alloys are one of the promising materials for hydrogen storage application in alkaline cells due to their high activity, high hydrogen capacity and low cost. It is reported that hydrogen storage materials could be prepared by using different techniques. Alloying and microstructure modification (refining) are the main approaches to improve the hydrating properties. Mechanical alloying (MA) [1-3] and melt-spinning [4,5] are proved to be extremely appropriate techniques for producing Mg-based amorphous and nanocrystalline materials in a large range of composition. Recently, MA has been reported to be an efficient method for synthesizing novel materials with special physical and chemical properties. Furthermore, the MA process, structure and properties of materials formed with MA have been discussed in the literature [6,7]. Thus, the production of hydrogen with novel processes has attracted much attention. In our present work, we focused our attentions on the synthesis of $Mg_{67}Ni_{15}Y_9Al_9$ alloy with using MA method, as well as the discussion of the microstructure and electrochemical performance.

Experimental Procedures

The elemental powders of Mg (3N, 30 mesh), Ni (4N, 150 mesh) Y(3N, 50 mesh) and Al (4N, 100 mesh), were used. Mechanical alloying (MA) was carried out in a vibratory ball mill at a vibration frequency of 25 Hz. The stainless steel vial with ZrO_2 lining and ZrO_2 balls were utilized. The milling was conducted in argon atmosphere for 0-200 hour. The powder handling was done in an argon-filled glove box. The alloyed powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC)

The well-mixed alloy powders were pressed into the tablets as metal hydride electrode, and the electrochemical properties were then measured in a standard electrode cell consisting of a working electrode and a conter-electrode $NiOOH/Ni(OH)_2$ electrode. The electrolyte in the cell was 6M KOH aqueous solution. Charge and discharge tests were carried out on an automatic galvanostatic system at room temperature. The experimental cell was firstly charged at current of 60 mA for 5.5 hours followed by a rest of 30 minutes and then discharged at the same discharge current density to the cut off voltage of -0.60 V.

Results and Discussions

Structure Characteristics of Synthesized Powders

Fig.1 shows the SEM images of the as-milled $Mg_{67}Ni_{15}Y_9Al_9$ powders after different milling times. At 19 h of milling as shown in Fig. 1b, the as-milled powders exhibited larger particles, and the particle size decreased gradually with increasing milling time. After 200 h of milling, the well-proportioned powders were formed and the size of the particle is less than 20 μm (Fig. 1d).

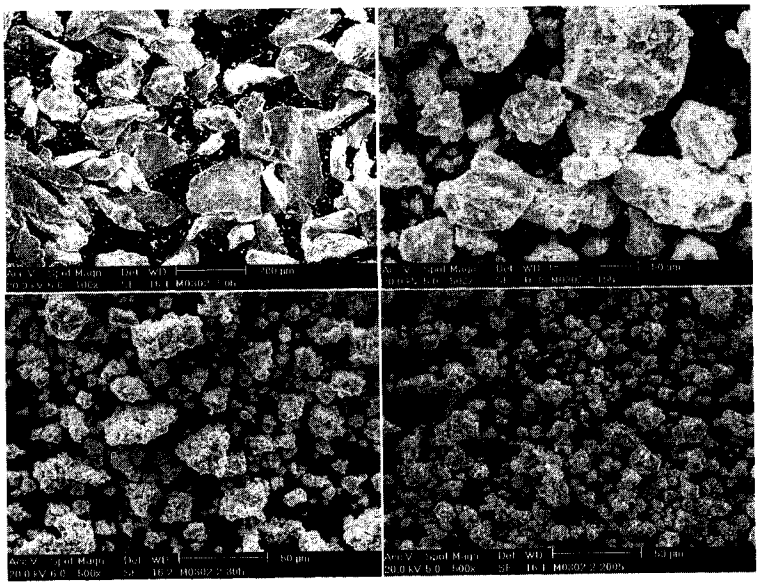

Fig. 1. SEM images of as-milled $Mg_{67}Ni_{15}Y_9Al_9$ powders after different milling times. (a) MA for 0 h, (b) MA for 19 h, (c) MA for 80 h and (d) MA for 200 h

The XRD patterns of the as-milled $Mg_{67}Ni_{15}Y_9Al_9$ powders as a function of milling time are shown in Fig. 2. At 19 and 80 h of milling, a large amount of crystalline Mg_2Ni phase was obtained (Fig. 2b and c). The peaks intensities of Mg_2Ni phase decreased and amorphous phase increased gradually with increasing milling time. After milling for 200 h, the as-milled powders mainly include a major amorphous phase and minor Mg_2Ni phase (Fig. 2d).

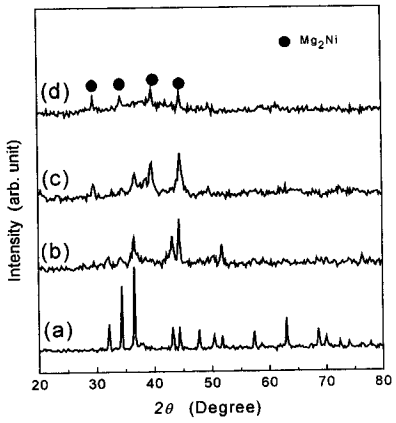

Fig. 2. XRD patterns of $Mg_{67}Ni_{15}Y_9Al_9$ mixtures milled for different times under Ar atmosphere. (a) MA for o h, (b) MA for 19 h, (c) MA for 80 h and (d) MA for 200 h

For most of the amorphous alloy powders prepared by MA starting from elementary powder mixtures, the elemental XRD peaks decreased gradually during the early milling stage which is similar to that observed during the amorphization by MA in many systems. At the early stage, the diffraction peak intensities of the elements decreased and a broad peak intensity of the amorphous alloy increased. At the final stage, intermetallic compounds were formed as intermediate products and further milling resulted in amorphous and crystalline phases. In the current study, as shown in Fig. 2, the diffraction peaks for the Mg_2Ni phase on the a broad diffraction peak of amorphous phase were formed after MA for 200 h (Fig. 2d) of milling, it suggested that the amorphization reaction is mainly responsible for the formation of as-milled $Mg_{67}Ni_{15}Y_9Al_9$ powders.

Thermal Stability of As-milled Powders

The exothermic behavior of $Mg_{67}Ni_{15}Y_9Al_9$ powder as-milled for 200 h was investigated by DSC at a heating rate of 0.67 Ks^{-1} and the results are shown in Fig. 3. It can be seen that the as-milled state (amorphous and Mg_2Ni phases) changes to the crystalline state, exhibited by a broad exothermic reaction at the onset transition temperature (T_x) at about 660 K, which indicated a phase transformation from amorphous to the crystallization, followed by an endothermic peak with the melting temperature range of the solidus temperature (T_s) to the liquidus temperature (T_l) around 740-770 K.

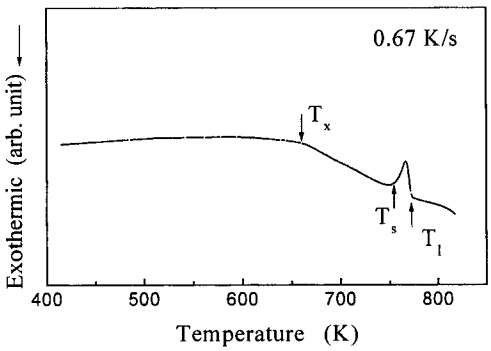

Fig. 3. DSC heating trace of as-milled $Mg_{67}Ni_{15}Y_9Al_9$ powders after MA for 200 h

Electrochemical Properties

Recently, studies on the electrochemical properties of Mg-based alloy have received more attention. In this work, the electrochemical charge and discharge capacity has been measured. The first charge/discharge curves of mechanically alloyed $Mg_{67}Ni_{15}Y_9Al_9$ powder electrode are depicted in Fig. 4. It shows that the $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode exhibits activation characteristics. Under this experimental condition, the discharge capacity of the alloy prepared by MA was 52 $mAhg^{-1}$ at the first cycle.

The change of the electrochemical discharge capacities of $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode with increase in cycle numbers are shown in Fig. 5. It shows that the $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode reaches a maximum discharge capacity of 52 $mAhg^{-1}$ at the first electrochemical charge/discharge cycle, and the discharge capacity decreases during the cycling test, it decreases to 22 $mAhg^{-1}$after 21th cycle.

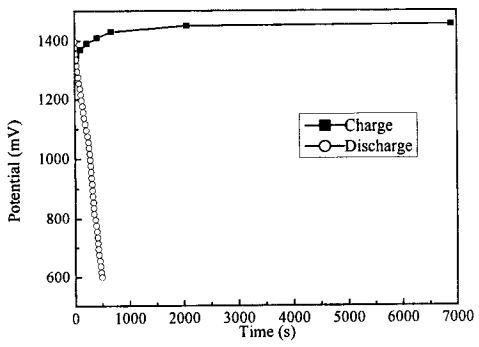

Fig. 4. Electrochemical charge/discharge curves of $Mg_{67}Ni_{15}Y_9Al_9$ alloy after MA for 200 h powders electrode in 6M KOH solution

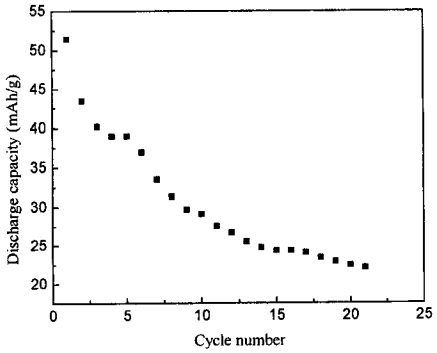

Fig. 5. Electrochemical discharge capacities as a function of the cycle number for $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode

Mechanism of the Cyclic Stability

From electrochemical measurements, the as-milled powder electrode studied has shown that the discharge capacity decreases during the cycling test. In order to investigate the reason for the discharge capacity loss of the $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode during the electrochemical

charge/discharge cycling, XRD analysis for the electrode was carried out, and the results are depicted in Fig. 6. It shows a peak of Mg_2NiH_4 and $Mg(OH)_2$ phases after 21th charge/discharge cycle. It is supposed that Mg on the surface of as-milled $Mg_{67}Ni_{15}Y_9Al_9$ particles were oxidized to $Mg(OH)_2$ during the charge/discharge cycles in 6M KOH solution, which results in the decrease of discharge capacity.

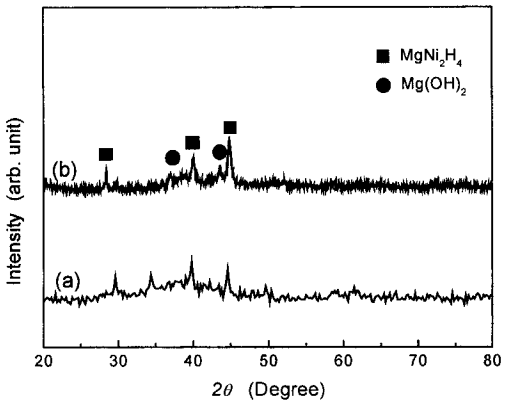

Fig. 6. XRD patterns of the $Mg_{67}Ni_{15}Y_9Al_9$ electrode after different cycles. (a) Before charge/discharge, (b) After 21th cycle

It is important to compare the electrochemical discharge capacity of the Mg-based alloys electrode with its amorphous or crystalline counterpart. The electrochemical discharge capacity is 10-15 $mAhg^{-1}$ for the amorphous $Mg_{52-62}Ni_{33}La_{5-10}$ alloys after 5th cycle [5] and 25 $mAhg^{-1}$ for the crystalline $Mg_{1.9}Y_{0.1}Ni_{0.9}Al_{0.1}$ alloy after 50th cycle at discharge current density of 10 mAg^{-1} [8]. The value of the electrochemical discharge capacity is 22 $mAhg^{-1}$ after 21th cycle at discharge current density of 60 mAg^{-1} for the present amorphous and crystalline $Mg_{67}Ni_{15}Y_9Al_9$ alloy. It is still a challenge to improve the electrochemical discharge capacity and cyclic life property for amorphous/crystalline Mg-based alloys.

Summary

A powder material of $Mg_{67}Ni_{15}Y_9Al_9$ was synthesized by the mechanical alloying method. Considerable amounts of amorphous and microcrystalline phases were formed after a mixture of elemental powder was mechanical alloyed for 200 h. The well-proportioned powders were formed with a particle size less than 20 μm.

The as-milled $Mg_{67}Ni_{15}Y_9Al_9$ alloy electrode presented a maximum discharge capacity of 52 $mAhg^{-1}$ at the first electrochemical charge/discharge cycle then decreased during the cycling tests. It was decreased to 22 $mAhg^{-1}$ after the 21th cycle, which is attributed to the formation of $Mg(OH)_2$ on the electrode surface.

Acknowledgements

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