Journal of Alloys and Compounds 555 (2013) 131–137

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Comparative study of electrochemical performances of the as-melt $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; x = 0, 4) alloys applied to Ni/metal hydride (MH) battery

Yanghuan Zhang [a,b,*], Chen Zhao [a,b], Tai Yang [a,b], Hongwei Shang [a,b], Chao Xu [a,b], Dongliang Zhao [b]

[a] Key Laboratory of Integrated Exploitation of Baiyun Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou 014010, PR China
[b] Department of Functional Material Research, Central Iron and Steel Research Institute, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form 3 December 2012
Accepted 6 December 2012
Available online 12 December 2012

Keywords:
Mg_2Ni-type alloy
Element substitution
Melt spinning
Nanocrystalline and amorphous
Electrochemical characteristics

ABSTRACT

The partial substitution of M (M = Cu, Co, Mn) for Ni has been performed in order to ameliorate the electrochemical hydrogen storage performances of Mg_2Ni-type electrode alloys. The melt spinning technology was used to prepare the $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; x = 0, 4) electrode alloys. The impacts of the melt spinning and the M (M = Cu, Co, Mn) substitution on the structures and electrochemical hydrogen storage characteristics of the alloys were investigated systemically. The analysis of XRD and TEM reveals that the as-spun (M = None, Cu) alloys display an entire nanocrystalline structure, whereas the as-spun (M = Co, Mn) alloys hold a nanocrystalline/amorphous structure, indicating that the substitution of M (M = Co, Mn) for Ni facilitates the glass formation in the Mg_2Ni-type alloys. Besides, all the as-cast alloys have a major phase Mg_2Ni, whereas the M (M = Co, Mn) substitution brings on the formation of some secondary phases, $MgCo_2$ and Mg for the (M = Co) alloy, and MnNi and Mg for the (M = Mn) alloy. Based upon the electrochemical measurements, an evident impact engendered by melt spinning on the electrochemical performances of the alloys appears. The cycle stability of the alloys augments monotonously with the growing of the spinning rate. The discharge capacity and high rate discharge ability (HRD), however, act differently. Melt spinning enhances the cycle stability of the (M = Co, Mn) alloys dramatically, but exerts an adverse impact on the (M = None, Cu) alloys. The high rate discharge ability (HRD) of all the alloys grow considerably with the rising of the spinning rate except for (M = Mn) alloy, whose HRD has a maximum value with the variation of the spinning rate. Furthermore, the substitution of M (M = Cu, Co, Mn) for Ni enhances the electrochemical performances of the as-cast and spun Mg_2Ni alloys evidently, but the M (M = Mn) substitution gives rise to a decline of HRD when the spinning rate reaches 20 m/s.

1. Introduction

Mg_2Ni-type metallic hydrides are looked upon as one of the most promising negative electrodes applied to Ni-MH batteries [1,2] or hydrogen storage materials because of their major advantages, such as the theoretical electrochemical capacity being 1000 mAh/g and gaseous hydrogen absorption capacity being 3.6 wt.% for Mg_2NiH_4 [3,4]. However, the practical application of these alloys is deeply frustrated by their relatively high hydrogen-desorption temperatures, sluggish hydriding/dehydriding kinetics as well as extremely poor electrochemical cycle stability. In fact, the specific capacity and hydriding/dehydriding kinetics of hydride electrode materials depend on their chemical composition and crystalline structure [5,6]. It was documented that Mg and Mg-based hydrogen storage alloys with a nanocrystalline/amorphous structure exhibit higher hydrogen-absorption capacity and faster hydriding/dehydriding kinetics than crystalline Mg_2Ni [7].

High energy ball-milling (HEBM) is undoubtedly deemed to be a quite effective method for preparing nanocrystalline/amorphous Mg and Mg-based alloys [8]. However, the milled Mg and Mg-based alloys exhibit rather poor cycle stability owing to the vanishment of the metastable structures formed by ball milling during the multiple electrochemical charging and discharging cycles [9], which is an insurmountable barrier for its practical application as electrode materials. Alternatively, the melt spinning technique not only overcomes the aforementioned shortcomings but also prohibits the rapid degradation of the hydrogen absorbing/desorbing cyclic characteristics of Mg and Mg-based compounds [10]. Huang et al. [11] reported that the nanocrystalline/amorphous $(Mg_{60}Ni_{25})_{90}Nd_{10}$ alloy prepared by melt spinning yields its highest discharge capacity of 580 mAh/g. Spassov and Köster [12] prepared

* Corresponding author at: Department of Functional Material Research, Central Iron and Steel Research Institute, 76 Xueyuan Nan Road, Haidian District, Beijing 100081, PR China. Tel.: +86 010 62183115; fax: +86 010 62187102.
E-mail address: zyh59@yahoo.com.cn (Y. Zhang).

0925-8388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2012.12.016

$Mg_{63}Ni_{30}Y_7$ hydrogen storage alloy by rapid solidification process, obtaining a maximum hydrogen absorption capacity of about 3.0 wt.%. In addition, the as-spun Mg_2(Ni, Y) alloys demonstrated an enhanced hydriding kinetics compared to the conventionally prepared polycrystalline Mg_2Ni alloys, even comparable to that of the ball-milled nanocrystalline Mg_2Ni.

It was documented that the partial substitution of some elements (Cu, Fe, V, Cr, Co) for Ni in Mg_2Ni compound decreases the stability of the hydride and makes the desorption reaction easier [13,14]. Besides, such substitution facilitates the glass forming of the Mg_2Ni alloy. In which a single amorphous phase can be obtained by adding a small amount of La, Y or Nd [11]. Based on these results, the present investigation is focused on the influences of substituting M (M = Cu, Co, Mn) for Ni and melt spinning on the structure and electrochemical hydrogen storage performances of Mg_2Ni-type alloys. In this study, the Mg_2Ni-type $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; $x = 0, 4$) alloys were synthesized by melt spinning technology. Afterwards, we made a general comparison of the impacts on the structure and the electrochemical performances generated by element substitution and melt spinning.

2. Experimental

The compositions of the experimental alloys were $Mg_{20}Ni_{10-x}M_x$ (M = Cu, Co, Mn; $x = 0, 4$). The alloy ingots were prepared by using a vacuum induction furnace in a helium atmosphere at a pressure of 0.04 MPa to prevent Mg from volatilizing. A part of the as-cast alloys was re-melted and spun by melt spinning with a rotating copper roller cooled by water. The spinning rates used in the experiment were 15, 20, 25 and 30 m/s, respectively, which were approximately expressed by the linear velocity of the copper roller.

The phase structures of the as-cast and spun alloys were determined by X-ray diffraction (XRD) (D/max/2400). The diffraction, with the experimental parameters of 160 mA, 40 kV and 10°/min respectively, was performed with $CuK_{\alpha 1}$ radiation filtered by graphite.

The thin film samples of the as-spun alloys prepared by using ion etching technology were observed by high resolution transmission electron microscope (HRTEM) (JEM-2100F, operated at 200 kV).

The as-cast and spun alloy powders ground mechanically was filtered by a sieve with the mesh of 20 μm. The alloy powder and carbonyl nickel powder were mixed in a weight ratio of 1:4. The mixture was cold pressed under a pressure of 35 MPa into round electrode pellets with 15 mm in diameter and 1 g in weight.

The electrochemical measurements were performed at 30 °C by using a tri-electrode open cell consisting of a working electrode (the metal hydride electrode), a sintered $Ni(OH)_2$/NiOOH counter electrode as well as a Hg/HgO reference electrode, which were immersed in 6 M KOH electrolyte. The voltage between the negative electrode and the reference one was defined as the discharge voltage. In every cycle, the alloy electrode was first charged with a constant current density, after resting for 15 min, it was discharged at the same current density to cut-off voltage of −0.500 V.

The electrochemical impedance spectra (EIS) and the Tafel polarization curves of the alloys were measured by an electrochemical workstation (PARSTAT 2273). The fresh electrodes were fully charged and then rested for 2 h up to the open circuit potential stabilization. For the EIS measurement, the frequency ranged from 10 kHz to 5 mHz at 50% depth of discharge (DOD), the amplitude of signal potentiostatic or galvanostatic measurements being 5 mV, the number of points per decade of frequencies being 60. For the Tafel polarization curves, the potential range was −1.2 to +1.0 V (vs. Hg/HgO) with a scan rate of 5 mV/s. For the potentiostatic discharge, the test electrodes in the fully charged state were discharged at 500 mV potential steps for 3500 s on electrochemical workstation (PARSTAT 2273), using the electrochemistry corrosion software (CorrWare).

3. Results and discussion

3.1. Microstructure characteristics

Fig. 1 depicts the XRD profiles of the as-cast and spun $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; $x = 0, 4$) alloys. The as-cast (M = None, Cu) alloys hold a single phase structure, whereas the (M = Co, Mn) alloys have secondary phases, being $MgCo_2$ and Mg for the former, MnNi and Mg for the latter, indicating that such substitution generates secondary phases. Also, the diffraction peaks of the as-spun (M = None, Cu) alloys display an entire crystal structure, while the peaks of the as-spun (M = Co, Mn) alloys are much broader around 40° ascribed to the mixture of nanocrystalline/amorphous structure, suggesting that the substitution of M (M = Co, Mn) for Ni facilitates the glass formation in the Mg_2Ni-type alloy.

Fig. 2 demonstrates the TEM micrographs of the as-spun (30 m/s) $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; $x = 0, 4$) alloys. Evidently, the as-spun (M = None, Cu) alloys exhibit a nanocrystalline structure, and some crystal defects such as sub-grains and grain boundaries can be seen clearly from the amplified morphologies of

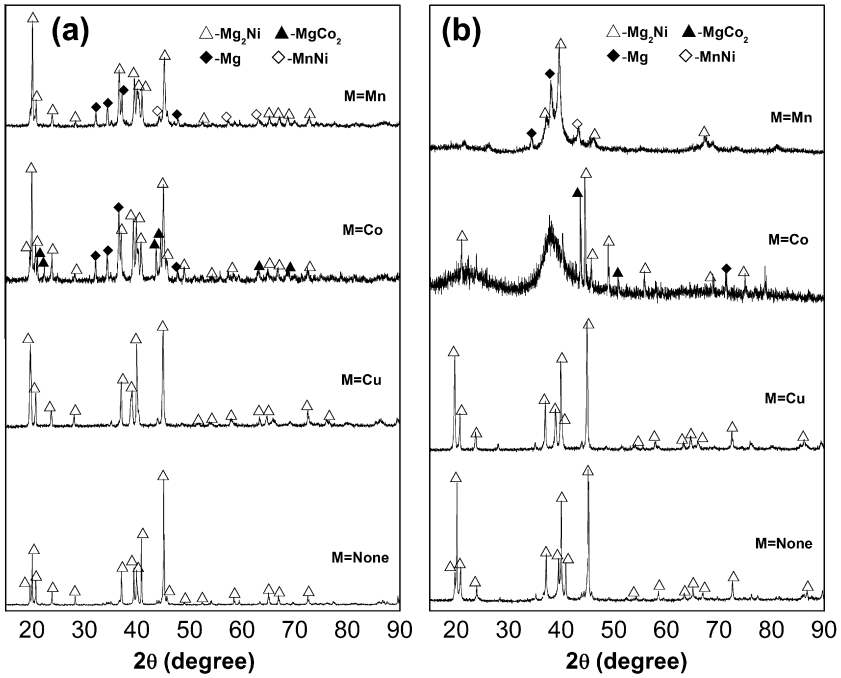

Fig. 1. XRD profiles of the as-cast and spun $Mg_{20}Ni_{10-x}M_x$ (M = None, Cu, Co, Mn; $x = 0, 4$) alloys: (a) as-cast and (b) as-spun (30 m/s).