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ScienceDirect
International Journal of Hydrogen Energy 32 (2007) 2830–2835
International Journal of HYDROGEN ENERGY
www.elsevier.com/locate/ijhydene

Electrochemical characteristics of mechanical alloyed $(Mg_{1-x}Zr_x)_2Ni$ $(x=0–0.1)$ electrode alloys

Yang-huan Zhang[a,b,*], Dong-liang Zhao[a], Xiao-ying Han[a], Bao-wei Li[b],
Xiao-ping Dong[a,c], Xin-lin Wang[a]

[a]Department of Functional Material Research, Central Iron and Steel Research Institute, 76 Xueyuan Nan Road, Haidian District, Beijing 100081, China
[b]School of Material, Inner Mongolia University of Science and Technology, Baotou 014010, China
[c]School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

Received 19 November 2006; received in revised form 16 January 2007; accepted 16 January 2007

Abstract

The electrode alloys $(Mg_{1-x}Zr_x)_2Ni$ $(x=0, 0.1)$ were prepared by mechanical alloying (MA). Mg in the alloy was partially substituted with Zr in order to improve the electrochemical characteristics of the Mg_2Ni-type alloy. The microstructures and the electrochemical characteristics of the experimental alloys were measured systemically. The effects of substituting Mg with Zr as well as the relevant MA technique on the microstructures and electrochemical performances of the alloys were investigated in detail. The results show that the substitution of Zr is favourable for the formation of an amorphous phase. The electrochemical measurement indicated that the substitution of Zr can dramatically enhance the discharge capacity and cycle stability, and it markedly improves the discharge voltage characteristic of the alloys. For a fixed alloy, the electrochemical performances, including the cycle stability, the discharge voltage characteristic and discharge capacity, of the alloys were significantly improved with the increase of the ball-milling duration.

Keywords: Mg_2Ni-type electrode alloy; Mechanical alloying; Microstructure; Electrochemical characteristic

1. Introduction

In recent years, considerable attention has been paid to the research of Mg-based alloys, particularly the amorphous Mg_2Ni-type alloys with different compositions prepared by mechanical alloying (MA) and mechanical grinding (MG). As a consequence, Mg_2Ni-type hydrogen storage alloys are considered to be promising energy conversion and storage materials. The polycrystalline Mg_2Ni phase, however, tends to form a stable hydride, Mg_2NiH_4, which is unable to desorb hydrogen at room temperature and shows a very low electrochemical discharge capacity [1,2]. Therefore, the pursuit of improving the hydrogen absorption/desorption kinetics of the Mg_2Ni-type alloy has been one of the main challenges faced by researchers in this field. For this purpose, the researchers in the world have carried out a lot of investigations and obtained some very important results. Lei et al. obtained improved discharge capacities of around 500 mAh/g for Mg_2Ni alloys prepared by MA at a current density of 20 mA/g [3]. Iwakura et al. [4] also improved the discharge capacity of Mg-based alloy with graphite surface modification by ball milling (BM). After surface modification with Ni powder by BM, Kohno et al. obtained a large discharge capacity of 750 mAh/g at a current density of 20 mA/g for modified Mg_2Ni alloys [5]. They proposed that the change of crystal grain size and the heterogeneous strain of Mg_2Ni alloy were responsible for the improvement in discharge capacity, and a small amount of crystalline Ni remained in the alloy may also work as a catalytic site for hydrogen dissociation on the surface. The theoretical discharge capacity of the Mg_2Ni phase, assuming the formation of the Mg_2NiH_4, is 999 mAh/g,

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[*] Corresponding author. Department of Functional Material Research, Central Iron and Steel Research Institute, 76 Xueyuan Nan Road, Haidian District, Beijing 100081, China. Tel.: +86 010 62187570; fax: +86 010 62182296.
E-mail addresses: zyh59@yahoo.com.cn, zhangyh59@163.com (Y.-H. Zhang).

0360-3199/$ - see front matter
doi:10.1016/j.ijhydene.2007.01.008

on which the worldwide researchers pay much attention. But its cycle life is so poor that only about 20% of the maximum capacity remains after 10 cycles. Obviously, there is a long way to impel the Mg_2Ni-type alloy from laboratory to market. The key problem is unchanged on how to improve the cycle stability of the alloy. It is well known that the element substitution is one of the effective methods for improving the overall properties of the hydrogen storage alloys [6]. The present work was focused on producing amorphous and nanocrystalline $(Mg_{1-x}Zr_x)_2Ni$ ($x = 0, 0.1$) alloys by MA and studying their hydrogen sorption properties. The microstructure and morphology of the milled powders were characterized as well.

2. Experimental

2.1. Preparation of alloy

Pure metal powders of magnesium, nickel and zirconium were used as starting materials, and the purity of all the component powders is at least 99.9%. The compositions of the mixed powders are stoichiometrically written as $(Mg_{1-x}Zr_x)_2Ni$ ($x = 0, 0.1$). Corresponding to Zr content x, the powders are represented by Zr_0 and Zr_1, respectively. Cr–Ni stainless steel balls and the mixed powders with a weight ratio of 35:1 were charged into Cr–Ni stainless steel vials together. The BM was performed with a laboratory planetary mill with milling durations of 10, 20, 30 and 40 h under argon atmosphere. The milling speed was 135 rpm. The samples were handled in a glove box under Ar and the vials were sealed under argon atmosphere. A small amount of the powder was taken from the mill at regular periods of time for structural, morphological and electrochemical measurement.

2.2. Microstructural analysis

The structures of the MA alloys were examined by a D/max/2400 X-ray diffractometer with Cu $K_{\alpha 1}$ radiation filtered by graphite. The experimental parameters for determining phase structure were 160 mA, 40 kV and 10°/ min, respectively. The structure of the amorphous phase was characterized by H-9000NA transmission electron microscopy equipped with an electron microprobe attachment. The morphologies of the MA alloy particles before and after electrochemical cycle were observed by JSM-6400 scanning electron microscopy.

2.3. Measurement of electrochemical performance

Round electrodes pellets of 15 mm in diameter were prepared by mixing 1 g MA alloy powder with fine nickel powder in a weight ratio of 1:1 together with a small amount of polyvinyl alcohol (PVA) solution as binder, and then compressed under a pressure of 35 MPa. After drying for 4 h, the electrode pellets were immersed in a 6 M KOH solution for 24 h in order to be fully wet before the electrochemical measurement. The experimental electrodes were tested in a tri-electrode open cell, consisting of a metal hydride working electrode, a $NiOOH/Ni(OH)_2$ counter electrode and a Hg/HgO reference electrode. The electrolyte was a 6 M KOH solution. The voltage between the negative electrode and the reference electrode is defined as the discharge voltage. In every cycle, the electrode was firstly charged with a constant current of 100 mA/g for 5 h, after resting 15 min, it was then discharged with 100 mA/g to a −0.500 V cut-off voltage. The environment temperature of the measurement was kept at 30 °C.

3. Results and discussion

3.1. Structural characteristics

The XRD patterns of the MA Zr_0 and Zr_1 alloy powders with different milling times were given in Fig. 1. Fig. 1(a) shows

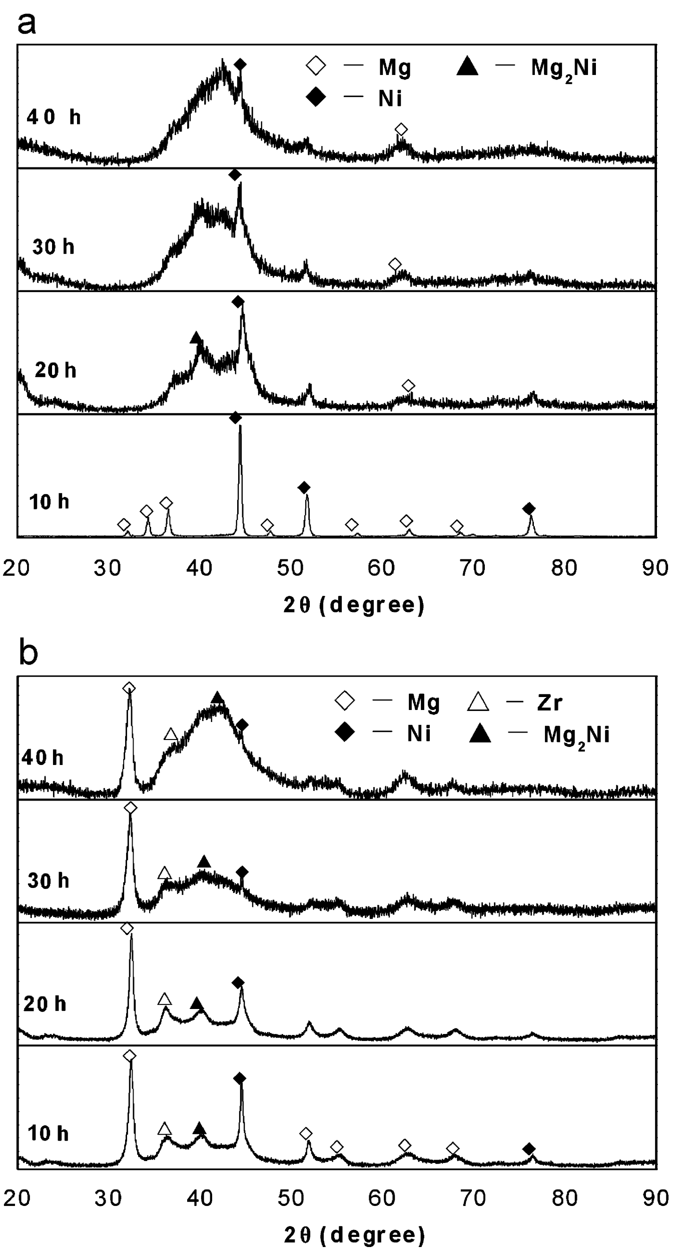

Fig. 1. The X-ray diffraction patterns of the MA alloys with different milling times: (a) Zr_0 alloy; (b) Zr_1 alloy.