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Effects of spinning rate on structures and electrochemical hydrogen storage performances of RE−Mg−Ni−Mn-based AB_2-type alloys

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Abstract: La was partially substituted by Ce with the aim of improving the electrochemical hydrogen storage performances of $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0, 0.1, 0.2, 0.3, 0.4) alloys, and melt spinning technology was adopted to fabricate the alloys. The identification of XRD and SEM reveals that the experimental alloys consist of a major phase $LaMgNi_4$ and a secondary phase $LaNi_5$. The growth of spinning rate results in that the lattice constants and cell volume increase and the grains are markedly refined. The electrochemical measurement shows that the as-cast and spun alloys can obtain the maximum discharge capacities just at the first cycle without any activation needed. With the increase of spinning rate, the discharge capacities of the alloys first increase and then decline, whereas their cycle stabilities always grow. Moreover, the electrochemical kinetic performances of the alloys first increase and then decrease with spinning rate growing.

Key words: Ni−MH battery; hydrogen storage; melt spinning; discharge capacity; kinetics

1 Introduction

Recently, an authoritative survey report from the Ministry of Environmental Protection of China declared that automobile exhaust is the main culprit giving rise to the severe haze in Beijing. Also, it was reported that a quarter of the world total energy was consumed by transport [1] and globally about 23% CO_2 emission originates from vehicular waste gases through the combustion of fossil fuels [2]. Hence, to vigorously develop electric vehicle (EV) and the hybrid electric vehicle (HEV) is deemed to be an attractive strategy to reduce both fossil energy consumption and carbon dioxide emission. To develop new electrode materials with high capacity, long life and low cost is a key technical obstacle for the widespread application of the EV and HEV. Several hydrogen storage materials are thought to be candidates as the negative electrode of Ni−MH batteries, especially rare earth-based AB_5 and AB_2-type alloys have been large-scale commercialized, but none of them is satisfactory due to their relatively low specific capacity. As for comprehensive electrochemical properties, RE−Mg−Ni-based A_2B_7-type and AB_2-type alloys have been considered to be the most promising candidates as the negative electrode materials of Ni−MH battery on account of their higher discharge capacities (380−410 mA·h/g) and lower production cost, as reported by KADIR et al [3] and KOHNO et al [4]. GUÉNÉE et al [5] studied the structures of $LaMgNi_4$ and $NdMgNi_4$ alloys and found that the alloys have a cubic $MgCu_4Sn$ ($AuBe_5$-type) structure. WANG et al [6] synthesized a $LaMgNi_4$ alloy by mechanical milling and found the maximum discharge capacity of the alloy being about 400 mA·h/g. Although extensive research has recently been performed to achieve the goal of application as summarized by LIU et al [7] and ZHANG et al [8], the attempt was still frustrated by the poor cycle stability of the new alloy. Consequently, the production of the new type alloys as the negative electrode of Ni−MH battery has not been found in China.

Alloying and microstructure modification are acknowledged to be effective approaches for improving the hydrogen storage properties of La−Mg−Ni-based

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alloy [9,10]. Particularly, the partial substitution of rare earth elements (Ce, Pr, Nd and Sm) for La and Co, Mn, Cu and Al for Ni can markedly ameliorate the electrochemical cycle stability of the alloys [11−13]. In addition, it is evidenced that the electrochemical performances of the alloys are very sensitive to their structures [14]. Our previous research results indicated that melt-spinning could dramatically refine the structure of the La−Mg−Ni system A_2B_7-type alloys and considerably improve their cycle stability [15]. Hence, we expect that the combination of an optimized Ce substitution amount with a proper melt spinning technique may obtain an alloy with high discharge capacity and good cycling stability.

It is documented that adding rare earth elements can significantly improve the corrosion resistance of an electrode material, so as to improve its electrochemical properties, especially the cycle stability [16]. However, the full effect of elemental substitution on the hydrogen storage properties of La−Mg−Ni-based AB_2-type alloy remains unknown. In the present work, Ce was adopted to partially substitute La because Ce is cheaper and more abundant in reserve than Y or other rare earth elements, and melt spinning technology was used to fabricate the $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0−0.4) alloys. Subsequently, the effects of spinning rate on the structure and electrochemical hydrogen storage characteristics of the alloys were investigated in detail. Our findings provide new insights into the capacity degradation mechanism of La−Mg−Ni system AB_2-type hydrogen storage alloys that may improve their cycling stability.

2 Experimental

The compositions of the experimental alloys were $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0, 0.1, 0.2, 0.3, 0.4). For convenience, the alloys were denoted with Ce content as Ce_0, $Ce_{0.1}$, $Ce_{0.2}$, $Ce_{0.3}$ and $Ce_{0.4}$, respectively. The as-cast alloys were prepared by vacuum induction melting with the protection of helium atmosphere under a pressure of 0.04 MPa. Then, the as-cast alloys were spun with a water-cooled rotating copper roller. The spinning rate was expressed by the linear velocity of the copper roller. In the present experiment, the spinning rates were 2, 6, 10 and 15 m/s, respectively.

The phase compositions and structures of the as-cast and spun alloys were evaluated by X-ray diffraction (XRD) (D/max/2400) with a scan rate of 4 (°)/min. Before the XRD testing, the alloys were mechanically ground into powders with size less than 300 μm. The morphologies of the alloys were examined by a scanning electron microscopy (SEM) (QUANTA 400) attached with an energy disperse spectroscopy (EDS).

The electrochemical performances were evaluated by using a tri-electrode open cell at 303 K. Metal hydride electrodes were prepared by pressing the alloy powders and carbonyl nickel powders at a mass ratio of 1:4. The total mass was about 1 g, and the diameter was 15 mm. A sintered $Ni(OH)_2$/NiOOH counter electrode, a Hg/HgO reference electrode and the prepared metal hydride electrode were immersed in 6 mol/L KOH electrolyte. The charge/discharge cycles were carried out with a LAND (CT2001A) battery test instrument. In every cycle, the experimental cells were charged at the current density followed by a rest for 10 min, and then were discharged at the same current density to cut off voltage of −0.5 V.

The electrochemical impedance spectra (EIS) and the Tafel polarization curves of the alloys were measured using an electrochemical workstation (PARSTAT 2273). The fresh electrodes were fully charged and then rested for 2 h up to the stabilization of the open circuit potential. The EIS values of the alloy electrodes were measured at 50% depth of discharge (DOD), in frequency range from 10 kHz to 5 mHz, at amplitude of signal potentiostatic or galvanostatic measurements being 5 mV and the number of points per decade of frequencies being 60. The Tafel polarization curves were measured in the potential range from −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 potential steps of 500 mV for 5000 s on electrochemical workstation, using an electrochemistry corrosion software (CorrWare).

3 Results and discussion

3.1 Microstructure characteristics

Figure 1 shows the XRD profiles of the as-cast and spun $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0−0.4) alloys. It reveals that the as-cast and spun alloys have biphasic structures with a major phase $LaMgNi_4$ corresponding to cubic $SnMgCu_4$ ($AuBe_5$)-type structure with $F\bar{4}3m$ (216) space group and the secondary phase $LaNi_5$ corresponding to hexagonal $CaCu_5$-type structure with $P6/mmm$ (191) space group. Also, it is noted that the diffraction profiles are similar and exhibit sharp peaks, indicating excellent crystallinities and long-range crystallographic orders of the alloys [17]. The melt spinning brings on an obvious variation in the phase abundances of the alloys without altering the phase composition. Table 1 shows the lattice parameters of the $LaMgNi_4$ and $LaNi_5$ phases in the as-cast and spun Ce_0 and $Ce_{0.2}$ alloys, which were calculated from the XRD data by Jade 6.0 software. It is evident that melt spinning makes the lattice constants and cell volumes of the $LaMgNi_4$ and $LaNi_5$ phases obviously increase, which is most likely associated with the lattice stress and crystal