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Structures and electrochemical performances of as-cast and spun RE-Mg-Ni-Mn-based alloys applied to Ni-MH battery

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ABSTRACT

The RE-Mg-Ni-Mn-based AB_2-type $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ ($x=0-0.4$) alloys were prepared by spinning treatment. For obtaining the optimum performance, the effects of Ce content and spinning rate on the hydrogen storage performance of the alloys were studied systematically. The results show that the variations of the spinning rate and Ce content result in noteworthy changes of the phase content without altering phase composition of the alloys. Specifically, the $LaMgNi_4$ phase increases and $LaNi_5$ phase decreases when increasing the spinning rate and Ce content. Furthermore, the crystalline grains of Ce-containing alloys prepared by spinning treatment are remarkably refined. The alloys own superior electrochemical performance. All alloys reach the optimal discharge capacity at the initial cycle. Increasing Ce content and spinning rate lead the discharge capacity and electrochemical kinetics rise to an optimal value and then start to reduce. Meanwhile, the electrochemical cycle stability is also improved, which is ascribed to the great enhancement of anti-pulverization and anti-corrosion abilities resulting from the spinning treatment and the substitution of Ce for La.

1. Introduction

The fossil fuel era will end "before long". Fortunately, mankind has come to realize the severity of the issue and start to initiatively give up fossil fuel and turn to investigate and use cleaner energy. Most of the developed countries have been pumping their funds into the development of the new energy auto industry. Some brands of the vehicles which take Ni-MH batteries as auxiliary power have already been sold in Europe, the United States and China. Therefore, the performances of Ni-MH batteries largely decide whether they will be accepted by the markets. As the core material, hydrogen storage materials fundamentally influence the main performances of Ni-MH batteries. However, at present, there is no ideal material that can meet the requirement of the vehicle batteries due to the low reversible capacity. The La-Mg-Ni type alloys have been extensively studied with the high reversible capacity and the low cost[1-6]. Unfortunately, the cycle stability of this type of alloys is poor, which has restricted their actual application process in vehicle batteries.

Alloying and modifying microstructure have been verified to be two powerful ways for enhancing the hydrogen absorption and desorption performance of the alloys[7-9]. Particularly, substituting partially rare earth elements for La and/or transition elements for Ni can make a marked amelioration on the electrochemical cycle stability[10-12]. In addition, the spinning treatment can also greatly refine the microstructure and dramatically enhance the cycle stability of the alloys[13,14]. Hence, RE-Mg-Ni-Mn-based alloys were prepared with different Ce contents and spinning rates for obtaining the alloys with the superior overall electrochemical performance.

It has been documented that adding rare earth elements Ce or Y can markedly enhance the corrosion resistance of an electrode and further improve its electrochemical properties, especially in the cycle stability[15-17]. In the present work, Ce was adopted to partially substitute La due to the fact that Ce is much cheaper than Y and other rare earth elements. And the spinning treatment was applied to prepare

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the $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ ($x=0-0.4$) alloys. The influences of Ce content and spinning rate on the microstructures and hydrogen storage performances were studied in detail.

2. Experimental

The as-cast $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ ($x=0-0.4$) alloys were prepared through melting the raw materials in a vacuum induction furnace. For avoiding the loss of Mg, the furnace was filled with helium gas of 0.04 MPa during the smelting process. The experimental alloys were denoted by Ce_0, $Ce_{0.1}$, $Ce_{0.2}$, $Ce_{0.3}$ and $Ce_{0.4}$ based on the different Ce contents. A part of the cast ingot was chosen as sample and spun to obtain the spun alloys. The linear velocity of the copper roller was used to represent the cooling rate of the alloys in the spinning treatment, which was set as 2, 6, 10 and 15 $m \cdot s^{-1}$, respectively.

X-ray diffractometer (XRD) (D/max/2400) was used to analyze the phase composition and content for the experimental alloys, and the test parameters were set as follows: 160 mA, 40 kV and 10 (°)/min, performing with CuKα1 radiation filtered by graphite. High resolution transmission electron microscope (HRTEM, JEM-2100F) was used to observe the microstructure of the spun alloys, and the working voltage was set to 200 kV. Electron diffraction (ED) was used to analyze the crystalline states.

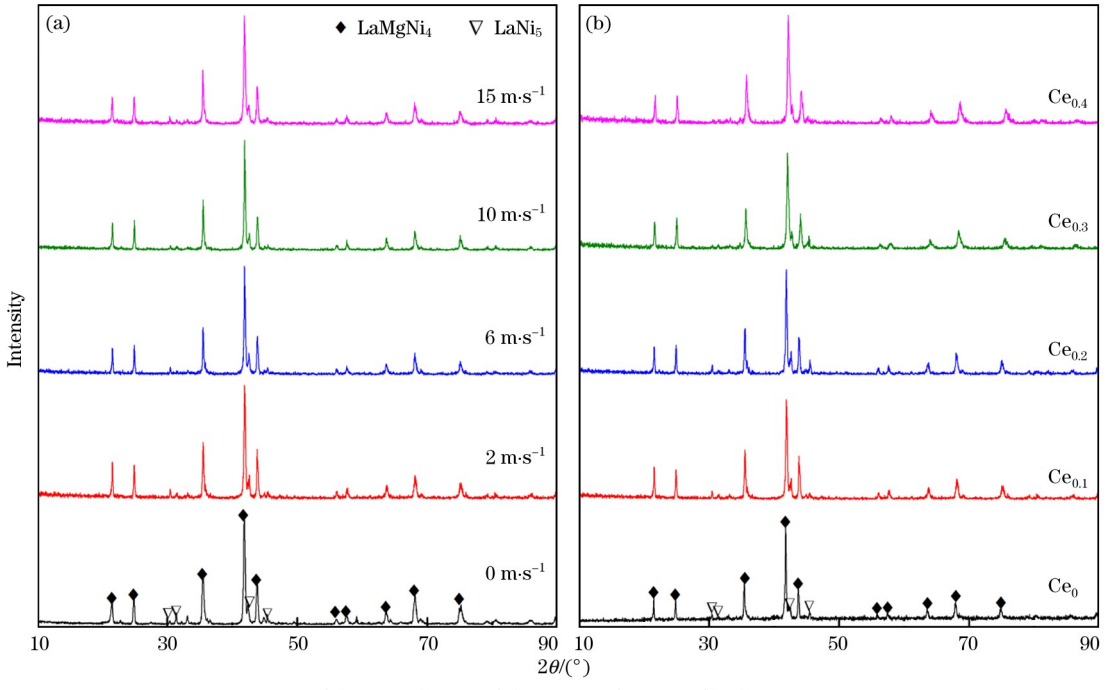
The alloy powder (0.2 g) and carbonyl nickel powder (0.8 g) were mixed and then pressed into ϕ15 mm round electrode at 35 MPa. The metal hydride electrode, sintered $Ni(OH)_2$/NiOOH counter electrodes as well as a Hg/HgO reference electrode jointly constituted a tri-electrode open cell which was infused with 6 $mol \cdot L^{-1}$ KOH electrolyte. The voltage between the metal hydride electrode and the Hg/HgO reference electrode was measured and defined as the discharge voltage. According to the general standard, the metal hydride electrode was first charged until the saturation state, held for 15 min, and then discharged until the voltage up to −0.500 V at a certain current density of 60 $mA \cdot g^{-1}$.

By using a PARSTAT 2273 type electrochemical workstation, the electrochemical kinetics of the alloys were tested. For measuring the electrochemical impedance spectra (EIS), the round electrode pellet was charged to 100%, held for 2 h, and then discharged to 50% depth of discharge (DOD). It was tested and recorded 60 points per decade in the frequency range from 10 kHz to 5 MHz at 5 mV of the amplitude of signal potentiostatic or galvanostatic measurements. The potentiostatic discharge of the saturated electrode was measured at 500 mV potential steps for 5000 s.

3. Results and Discussion

3.1. Microstructure characterization

The International Centre for Diffraction Data (ICDD) identification of the XRD patterns is presented in Fig. 1. There are a major phase $LaMgNi_4$ corresponding to the $SnMgCu_4$ structure and a secondary phase $LaNi_5$ phase. The differences of the spinning rate and Ce content bring on a remarkable variation in the ratio of $LaMgNi_4$ and $LaNi_5$ in the alloys. It is noted that the diffraction peak intensity of the $LaNi_5$



(a) $Ce_{0.1}$ alloys; (b) As-spun (2 $m \cdot s^{-1}$) alloys.

Fig. 1. XRD profiles of as-cast and spun $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ ($x=0-0.4$) alloys.