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Structures and electrochemical performances of RE-Mg-Ni-Mn-based alloys prepared by casting and melt spinning

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Abstract: La-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 melt spinning technology. The detections of X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that the experimental alloys consisted of a major phase $LaMgNi_4$ and a secondary phase $LaNi_5$. With spinning rate growing, the abundance of $LaMgNi_4$ phase increased and that of $LaNi_5$ phase decreased. Moreover, with the melt spinning rate increasing, both the lattice constants and cell volumes increased, and further accelerated the grains refinement of the alloys. The electrochemical tests showed that the as-spun alloys possessed excellent capability of activation, achieving the maximum discharge capacities just at the first cycling without any activation needed. As for the as-spun alloys, its discharge potential characteristics could be improved obviously by adopting the technology of melt spinning. In addition, the melt spinning raised electrochemical cycle stability of the alloys, the main reason was that the melt spinning enhanced the anti-pulverization ability of the alloys. With spinning rate increasing, the discharge capacity of the alloys presented a tendency to increase firstly then decrease. Moreover, the electrochemical kinetics of the alloys showed the same trend under fixed condition.

Keywords: AB_2-type alloy; Ce substitution for La; melt spinning; electrochemical performance; kinetics; rare earths

The rapid development of automobile industry brings quick and convenient life for people, but leads to excessive consumption of limited fossil fuels and a series of environmental problems. Especially, rapidly increasing global warming and air pollution have captured attention all over the world. An attractive strategy to reduce both fossil energy consumption and carbon dioxide emissions is convinced to vigorously develop electric vehicle (EV) and the hybrid electric vehicle (HEV). Some investigations and statistical results showed 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]. Recently, an authoritative survey report from the Ministry of Environmental Protection of China declared that automobile exhaust is the main culprit resulting in the severe smog in Beijing. Actually, the Ministry of Industry and Information Technology of China has enacted “The regulation of access of new energy automobile production enterprises and products” as early as 2009, noted that the hybrid-electric vehicles (HEV) in which nickel-metal hydride battery is adopted as assistant energy have faced the world market, and been made into mature products for selling. In addition, hydrogen storage alloys have long been voted the most promising to become the negative electrode of nickel-hydrogen batteries. Especially rare earth-based AB_5 and AB_2-type alloys have been large-scale commercialized. However, none of them is satisfactory as the cathodal active substance of nickel-hydrogen battery because some of their inherent shortcomings, such as relatively low specific capacity for AB_5 alloy and difficult to be activated for AB_2 alloy. Considering the discharge capacity, since always, because of lower production cost and higher discharge capacities (from 380 to 410 mAh/g), the La-Mg-Ni-based of AB_2-type and A_2B_7-type alloys are considered most perspective practical materials as the cathodal active substance of Ni/MH battery[3,4], as Kohno[5] and Kadir et al.[6] reported. Liu et al.[7,8] have summarized the studying situations on how to achieve the goal of application in recent years. However, the studies were still no sign of a breakthrough in improving the poor cycle stability of the alloys.

Broadly speaking, the microstructure modification and alloying method proved to be two significant ways of improving the hydrogen storage properties of La-Mg-Ni-based AB_2-type alloy[9–11]. Besides, the rare earth elements (Pr, Nd, Sm and Ce) partially substituting for La and metallic elements (Co, Al, Cu and Mn) for Ni can markedly ameliorate the electrochemical cycle stability

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of the alloys[12–14]. And previous studies showed that Mn partial substitution for Ni can increase the cell volume, decrease the hydrogen plateau pressure, shorten the activation cycle and improve the high rate discharge ability[15,16]. In addition, previous studies have shown that melt-spinning can greatly refine the structures of the La-Mg-Ni system A_2B_7-type alloys and dramatically improve their cycle stability[17,18]. Hence, It is expected that the discharge capacity and cycle stability can be ameliorated by synergistic effect of the optimum doping content of Ce and a proper melt spinning technique.

It is generally known that adding rare earth elements Ce and Y can significantly improve the corrosion resistance of an electrode material, further improve its electrochemical properties, especially the cycle stability[19–21]. Because Ce is cheaper and more abundant than Y or other rare earth elements, in this work, we prepared the $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0–0.4) alloys by doping partial Ce into La with the melt spinning technology. The paper made a detailed study of the influences of Ce content on the structures and electrochemical hydrogen storage performances of the alloys.

1 Experimental

For convenience, the $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ (x=0, 0.1, 0.2, 0.3, 0.4) alloys were distinguished with Ce content as Ce_0, $Ce_{0.1}$, $Ce_{0.2}$, $Ce_{0.3}$ and $Ce_{0.4}$, respectively. The as-cast alloy was prepared by using vacuum induction melting method in a vacuum induction furnace. For avoiding the loss of Mg, helium was filled into the furnace about 0.04 MPa during melting operation. Then a part of the as-cast ingots were chosen as sample and melted to obtain the as-melted alloy on the surface of a rotating copper roller. Due to some experiment parameters, such as cooling rate of the sample and accurate spinning rate are hard to be gauged in the process of spinning, the copper roller linear velocity spinning rate was taken for spinning rate approximately. In this experiment, the spinning rates were set to be 2, 6, 10 and 15 m/s, respectively.

X-ray diffraction with Cu Kα radiation was performed in a Rigaku (D/Max-2400) diffractometer to determine the phase structure and compositions of the alloys, and performed using 40 kV, 100 mA and 10 (°)/min with Cu Kα radiation filtered by graphite. The lattice parameters and cell volumes of the phases were calculated using MDI Jade software. An SEM instrument (QUANTA 400) equipped with an energy dispersive spectrometer (EDS) was also employed to characterise the microstructure and micro-area chemical compositions of the as-cast alloy ingots.

The electrochemical performance of the alloy electrodes was determined using an automatic battery test instrument (LAND, CT2001A). The electrodes were prepared by pressing 0.200 g of alloy powders and 0.800 g of carbonyl nickel powders into pellets 15 mm in diameter under 25 MPa pressure. The primary role of the carbonyl nickel powder is conductive agent and binder. A metal hydride electrode was regarded as a working electrode, and a sintered $Ni(OH)_2$/NiOOH counter electrode was regarded as a positive electrode, combining with Hg/HgO reference electrode constituted a tri-electrode open cell which was infused with 6 mol/L KOH electrolyte and can be used for testing the performance of electrochemical kinetics. The voltage between metal hydride electrode and Hg/HgO reference electrodes was measured, and it can be selected as the discharge voltage. During each test cycle, firstly, the alloy electrode was charged, standing for 15 min, and then discharged until the voltage up to –0.500 V at a certain current density in each cycle. The discharge capacities of the alloys at different discharge current densities (60, 300, 600, 900, 1200 and 1500 mAh/g) were also measured to investigate their high-rate dischargeability (HRD).

The electrochemical kinetics of alloys and the potentiodynamic polarization curves of the alloys were measured at 303 K by using a PARSTAT 2273 type electrochemical workstation. For measuring the electrochemical impedance spectra (EIS), the round electrode pellet was charged to 100%, standing for 2 h to ensure a steady open circuit potential, and then discharged to 50% depth of discharge. 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. And the Tafel polarization curves were measured in the potential range of –1.2 to +1.0 V (versus Hg/HgO) with a scan rate of 5 mV/s. By using CorrWare electrochemistry corrosion software, the potentiostatic discharge of the saturated electrode was measured at 500 mV potential steps for 5000 s.

The micrographs of the alloy particles and phase compositions of the electrodes after 300 electrochemical cycles were also analyzed. The electrodes were mechanically crushed and characterized by SEM and XRD after drying in vacuum drying oven.

2 Results and discussion

2.1 Microstructure characterization

The ICDD identification of the XRD patterns displayed in Fig. 1 indicates that multiphase structures of the as-spun alloys consist of major phase $LaMgNi_4$ corresponding to the $SnMgCu_4$ ($AuBe_5$)-type structure with $F\bar{4}3m$ (216) space group and the secondary phase $LaNi_5$. The phase abundances of the alloys engender apparent improvement with the variation of spinning rate, but the phase compositions keep constant under the same condition. Through a careful observation, it is found that the