

Influence of rapid quenching on the microstructure and electrochemical properties of Co-free $\text{LaNi}_{4.92}\text{Sn}_{0.33}$ hydrogen storage electrode alloy

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Abstract

Co-free $\text{LaNi}_{4.92}\text{Sn}_{0.33}$ alloy samples were prepared by first induction melting and subsequent melt-spinning at different quenching rates, and their microstructure and electrochemical properties were comparatively investigated and compared. The results reveal that the as-cast alloy is of a coarse dendrite structure consisting of two distinct CaCu_5 major phases and a scattered minor Sn phase, has high volume expansion and pulverization rates on hydriding and noticeable composition segregation, resulting in a rather poor cycling stability ($S_{200} = 42.7\%$). However, the melt-spun alloys prepared at higher quenching rates are highly homogeneous in composition, of the single CaCu_5 phase in very fine cellular structure, have lower volume expansion and pulverization rates on hydriding, leading to a noticeably improved cyclic stability ($S_{200} = 62.5\text{--}78\%$), although their activation rate, initial capacity and high-rate dischargeability are slightly lowered. It is believed that the great improvement in cycling stability of the melt-spun alloys is mainly due to their lower degree of pulverization on hydriding and the higher uniformity in composition, and the relatively lower high-rate dischargeability is mainly due to the decrease in both the electrocatalytic activity and the hydrogen diffusion rate in the alloy bulk.

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Keywords: Hydrogen storage alloy; Co-free alloy; Rapid quenching; Microstructure; Electrochemical property

1. Introduction

AB_5 -type hydrogen storage alloys containing about 10 wt% Co are widely used as the negative electrode material of Ni/MH batteries because of their long cycle life and good overall properties. It is known that Co plays the prominent role in suppressing the pulverization and corrosion of the alloys during charge/discharge cycling, and thereby enhances the cycle life [1,2]. However, Co is expensive and drastically increases the alloy cost. Therefore, for reducing the alloy cost, many studies on the substitution of expensive Co with other low-cost elements (Cu, Fe, Si, Sn, etc.) have been carried out, and several low-Co or Co-free alloys were developed [3–6]. However, for commercial applications the cycling stability and overall electrode properties of these alloys have to be further improved. It has been found that the use of overstoichiometric alloys

(AB_{5+x}) is a promising way to reduce alloy corrosion [7–9], and many different material processing methods such as annealing treatment [10,11] and rapid quenching process [11–15] can also improve the cycling stability of the low-Co or Co-free alloys. Recently, it is reported that the annealed Co-free $\text{La}(\text{Ni}, \text{Sn})_{5+x}$ ternary alloys have good cycle life and storage capacities comparable to those of currently adopted AB_5 type alloys with 10 wt% Co, and thus these novel alloys have been regarded as good candidate for the low cost negative electrode materials for Ni/MH batteries [2,16]. In our previous study on the $\text{La}(\text{Ni}, \text{Sn})_{5+x}$ ($x = 0\text{--}0.4$) alloys, we found that the cycling stability of the alloys can be greatly improved by the increase of x value [17] and rapid quenching process of the alloys [18]. However, the effects of the rapid quenching treatment on the structural and electrochemical properties of the $\text{La}(\text{Ni}, \text{Sn})_{5+x}$ alloys have not been systematically studied so far, and it is worthy to be examined.

In this work, the overstoichiometric Co-free $\text{LaNi}_{4.92}\text{Sn}_{0.33}$ ($\text{AB}_{5.25}$) alloy was prepared first by induction melting and

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followed by a melt-spinning treatment at different quenching rates, the influence of the rapid quenching on their microstructure and electrochemical properties was comparatively investigated and compared.

2. Experimental

LaNi_{4.92}Sn_{0.33} alloy was prepared by induction melting in argon atmosphere and remelted three times to obtain a higher homogeneity. All starting elemental metals have purity higher than 99.9%. Subsequently the as-cast alloy ingots were remelted and quenched by melt-spinning method at different quenching rates, which was determined by the respective linear velocity of the rotating copper roller in the rapid quenching process. The suitable linear velocities used in this work were selected as 1, 3, 5 m/s.

The alloy samples thus prepared were ground mechanically into powder below 300 mesh and used for electrochemical tests and XRD analysis. The crystal structure of the alloy samples was determined by XRD analysis using a Rigaku D/max 2500/PC diffractometer with Cu K α radiation. These analyses were also made for the hydrided samples of the alloys under investigation. To avoid the desorption of hydrogen during measurement, the surface of electrochemically hydrided samples was coated with a glue layer. The microstructure and the composition of the samples were examined by using a scanning electron microscope (SEM) of Sirion-100 (FEI) and EDS.

For electrochemical tests, pellet type alloy electrodes ($d = 10$ mm) were prepared by cold pressing the mixtures of the alloy powder with carbonyl Ni powder in a mass ratio of 1:4 and the electrochemical tests were carried out at 298 K in a conventional tri-electrode cell consisting of a working electrode (MH electrode), a sintered Ni(OH)/NiOOH counter electrode and a Hg/HgO reference electrode, and the electrolyte was 6 M KOH solution. The discharge capacity was determined galvanostatically by using an automatic charge/discharge unit. Each electrode was charged at 100 mA/g for 4 h followed by a 10 min rest, and then discharged at 60 mA/g to the cut-off potential of -0.7 V (vs. Hg/HgO). The high rate dischargeability (HRD), defined as $C_i \times 100 / (C_i + C_{60})$, was determined from the ratio of the discharge capacity C_i (with $i = 300$ or 600 mA/g, respectively) to the total discharge capacity defined as the sum of C_i and C_{60} , which was the additional capacity measured subsequently at 60 mA/g after C_i was measured. The cycling tests were conducted at the charge/discharge current of 300 mA/g for 200 cycles. The cycling capacity retention rate S_{200} was defined as $S_{200}(\%) = C_{200} / C_{\max} \times 100$, where C_{200} was the discharge capacity at 200th cycles. In evaluating the kinetic properties of the electrode reaction, the linear polarization curves of the electrode were plotted with a Solartron SI 1287 potentiostat by scanning the electrode potential at the rate of 0.1 mV/s from -5 to $+5$ mV (versus open circuit potential) at 50% depth of discharge (DOD). The potentialstatic discharge technique was used to evaluate the diffusion coefficient of hydrogen within the alloy bulk. After being fully charged followed by a 30 min open circuit rest-period, the test electrodes were discharged with $+600$ mV potential-step for 4000 s on a Solartron SI 1287

potentiostat, with the CorrWare electrochemical/corrosion software.

3. Results and discussion

3.1. XRD analysis and microstructure

Fig. 1 shows the XRD patterns of the as-cast and melt-spun LaNi_{4.92}Sn_{0.33} alloys, and the lattice parameters of the alloys are listed in Table 1. It is found that the as-cast alloy is composed of a main phase with CaCu₅-type structure and a small amount of segregated Sn phase. Moreover, the main phase of the as-cast alloy is a mixture of two distinct CaCu₅ phases, consisting of a large amount of Sn-rich (LaNi_{~4.88}Sn_{~0.55}) phase (main CaCu₅ phase), along with a small amount of Sn-poor (LaNi_{~4.93}Sn_{~0.07}) phase (the second CaCu₅ phase marked with arrows). However, all the melt-spun alloys are of the single phase with CaCu₅ structure and contain no precipitation of the single Sn phase. This means that the high cooling rate of the melt-spinning process can effectively restrain Sn segregation in the alloy during solidification and promote the alloy to form single phase of CaCu₅ structure. In addition, the diffraction peaks for CaCu₅ phase become narrower and sharper after the alloy being quenched, indicating that the melt-spun alloys have a higher crystallinity and more relaxed lattice strain. As shown in Table 1, the melt-spun alloys have slightly larger c/a ratio and cell volume (V) as compared with the as-cast alloy, and the increase of quenching rate leads to a noticeable decrease in the expansion rate of cell volume ($\Delta V/V$) of the alloy on hydriding, decreasing from 19.3% for the as-cast alloy to the range of 18.3–17.1% for the 1–5 m/s melt-spun alloys. This result reveals that the cell volume expansion of the Co-free alloy induced by hydrogenation can be effectively decreased through a suitable rapid quenching treatment, and higher quenching rates adopted in this experiment all improve the anti-pulverization ability of the alloys during charge/discharge cycling.

Fig. 2 shows the SEM micrographs of the alloys. It can be seen that the as-cast alloy is of a coarse dendrite structure. After being quenched at the rate of 1 m/s, the alloy changes to a very fine dendrite structure. With increasing of quenching rate, the melt-spun alloys (3–5 m/s) are characterized by a very fine cellular structure. Evidently, the increase of quenching rates changes the way of crystal growth of the alloy and leads to a much smaller grain size.

Fig. 3 shows the scanning composition of La, Ni and Sn on sites every 0.34 μm apart along a horizontal straight line on the surface of these alloys by EDS analysis. The results show that the distribution of La, Ni and Sn in the melt-spun alloys is much more uniform in comparison with that in the as-cast alloy. This means that the melt-spinning process effectively improves the compositional homogeneity of the alloys.

3.2. Activation property and discharge capacity

The electrochemical properties of the alloys are summarized in Table 2. It can be seen that the as-cast alloy needs only two activation cycles (N_a) to reach its maximum discharge capacity

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