Phase Structure and Electrochemical Properties of Melt-Spun $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ Hydrogen Storage Alloys

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Abstract The ($\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$) alloys at different melt-spun speeds were prepared by using a vacuum melt-spun furnace, and the phase structure and electrochemical properties of alloys were studied. X-ray diffraction analysis results show that melt-spun $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys are composed of CeCu_5 -type, $\text{Pr}_5\text{Co}_{19}$ -type and CeNi_2 -type phase. As the melt-spun speed increased, the phase abundance of CeCu_5 -type increased, but that of $\text{Pr}_5\text{Co}_{19}$ -type decreased. Scanning electron microscopy–energy-dispersive spectroscopy analysis results show that melt-spun treatment can refine grain and make the alloys homogenization. Electrochemical tests show that all alloys have good activation performance within four cycles. With the increase in melt-spun speed, the cycle stability (S) of the alloys was improved obviously. After 100 cycles, the retention rate (S_{100}) of the alloy increased from 54.82% (as-cast) to 82.29% (25 m/s). Nevertheless, the maximum discharge capacity ($C_{\max}$) and high-rate dischargeability gradually decreased.

KEY WORDS: Hydrogen storage alloy; Melt-spun; Crystal structure; Electrochemical property

1 Introduction

To solve the energy crisis and the environmental pollution caused by fossil energy, various energy storage materials are widely studied and used, especially in the field of battery [1, 2]. Among these applications, MH/Ni battery shows an important part in the market due to their excellent performances, such as low cost, high energy density, high discharge capacity and renewable energy source. So far, several series storage of hydrogen alloys has been developed as negative materials of MH/Ni batteries. For

example, AB_5 -type alloys have been widely applied in Ni/MH batteries. However, it is still hard to meet the increasing demand for high-density energy [3–7]. In the past decade, La–Mg–Ni series alloys have gained extensive attention owing to their discharge capacity, which is higher than AB_5 -type alloys [8–11]. Nevertheless, La–Mg–Ni series alloys have poor cycle stability. Nowadays there are many ways to improve cycle life of hydrogen storage alloy electrode, such as element substitution [12–16], annealing treatment [12, 17, 18], rapid solidification technology [19–26] and surface treatment [27, 28]. Xu et al. [14] found that adding proper amount of Mn element in the A_2B_7 -type hydrogen storage alloy can improve the cycle stability of the alloy electrode. Zhang et al. [16] showed that the cycle stability and high-rate dischargeability can be improved by the adding of Mn content. Since the atomic radius of Mn is larger than Ni element, the cell volume and the lattice constant of alloy increase when Mn element partly replaces Ni element. Pan et al. [22] examined that the melt-spun treatment can refine grain and improve the cycle stability. Lin et al. [23] studied that the melt-spun alloys have

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excellent hydrogen absorption kinetics and low desorption temperature. Zhang et al. [24] reported that melt-spun treatment can improve the initial hydrogenation rate and the hydrogen absorption capacity of $\text{Mg}_{20-x}\text{La}_x\text{Ni}_{10}$ ($x = 0, 2$) alloys observably. It also illustrated the discharge capacity and the cycle stability of the alloys grew with the increase in the melt-spun speed. As is known, the Mg is easily volatile during melting. To minimize the burning loss of La and Mg, studies on melting and ICP analyses were carried out in our previous work. It is found that the burning loss of La and Mg can be minimized to 1% and 8% by using intermediate alloys (La–Mg, Mg–Ni and La–Ni). In this study, $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys were firstly prepared by intermediate alloys and then melt-spun at different speeds. The effects of rapid speed on the phase structure and electrochemical properties were discussed in detail.

2 Experimental

Alloy samples were prepared by vacuum induction levitation melting furnace (argon protection). The purity of the raw materials used in the preparation of alloys was greater than 99.9%. The ingots were re-melted and melt-spun speeds were 10, 15, 20 and 25 m/s, respectively. Based on our previous work, excess of Mg (8%) and La (1%) were added to the alloys to compensate for the evaporative loss.

The prepared alloy samples were mechanically ground into powder below 45 μm for X-ray diffraction (XRD) analysis and electrochemical tests. The phase identifications were performed on a Rigaku D/max 2500/PC diffractometer using $\text{CuK}\alpha$ radiation at a scan step of $3^\circ/\text{min}$, and the diffraction data ranging from 18° to 75° were collected. The results were calculated by Jade 6.5 software. Alloy electrode was a pellet with 1 cm in diameter, and total mass of about 0.5 g, which was prepared by cold pressing the uniform mixture of alloy powder and carbonyl nickel powder at the mass ratio of 1:4 under 15 MPa pressure. The electrochemical tests were carried out in a standard tri-electrode electrolysis cell at 25°C . The electrode cell consists of working electrode, a sintered $(\text{Ni}(\text{OH})_2/\text{NiOOH})$ counter electrode and a Hg/HgO reference electrode, and the electrolyte was 6 mol L^{-1} KOH solution. The discharge capacities and cycle stability of the alloy electrodes were measured galvanostatically by using an automatic charge/discharge unit. After charged at 120 mA g^{-1} for 4 h, each electrode was followed by rest of 5 min and then discharged at 60 mA g^{-1} to a cutoff potential of -0.7 V (vs. Hg/HgO). The charge/discharge current of the cyclical stability test was 300 mA g^{-1} . The high-rate dischargeability of the alloy electrode was characterized by $\text{HRD}_d = C_d/(C_d + C_{60}) \times 100\%$, where C_d is

the discharge capacity at the current densities of d ($d = 300, 600, 900\text{ mA g}^{-1}$) and C_{60} is the residual discharge capacity at the current density of 60 mA g^{-1} . The cycle stability of the alloy electrode was characterized by S_n (capacity retention rate) $= C_n/C_{\text{max}} \times 100\%$, where C_{max} is the maximum discharge capacity and C_n is the discharge capacity after n charge/discharge cycles. The linear polarization, exchange current density, electrochemical impedance and constant potential step were measured by a CS310 electrochemical workstation system.

3 Results and Discussion

3.1 Structure Characteristics

Figure 1 shows the XRD patterns of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ melt-spun and as-cast alloys. As shown in Fig. 1, the alloys are composed of CaCu_5 -type phase (space group: $\text{P6}/\text{mmm}$), $\text{Pr}_5\text{Co}_{19}$ -type phase (space group: $\text{P63}/\text{mmc}$) and CeNi_2 -type phase (space group: Fd-3 m). The peak intensity of $\text{Pr}_5\text{Co}_{19}$ -type phase decreases with the increase in melt-spun speed, which means that the melt-spun treatment can decrease the content of $\text{Pr}_5\text{Co}_{19}$ -type phase.

Figure 2 shows the XRD Rietveld analysis patterns of 15 m/s alloy, in which the fitting factor (R_{wp}) is 19. The fitting results reveal that the Mg occupies the $4f$ and $6c$ positions of La atom in A_5B_{19} -type structure, with the same occupation as Mg in PuNi_3 structure [13]. The unit cell parameters, phase composition and phase abundance of the alloy were calculated by the Rietveld method and are listed in Table 1. Table 1 shows that the phase abundance of CaCu_5 -type phase increases gradually from 48.2% (as-cast) to 63.1% (25 m/s), while that of $\text{Pr}_5\text{Co}_{19}$ -type phase in the alloy decreases from 30.1% (as-cast) to 22.9%

Fig. 1 XRD patterns of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ melt-spun and as-cast alloys

Fig. 2 XRD patterns for $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy (15 m/s)

(25 m/s). The cell volume of CaCu_5 -type phase in the alloy decreases with the increase in the melt-spun speed. Melt-spun treatment results in the grain refinement of the alloy sample without changing constituents of the alloy.

3.2 Structure Morphology

The typical results by SEM-EDS (energy-dispersive spectroscopy) of the $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys (as-cast, 10 m/s) are shown in Fig. 3. It can be seen that the alloys possess dendritic structure and the melt-spun treatment can refine grain and homogenize constituent of the alloy.

Comparing the EDS results of Fig. 3a with b, it can be seen that the element distribution of the melt-spun alloy (10 m/s) is more homogeneous than that of as-cast alloy, especially the Mg element. The refined grains have more grain boundaries, which improves the mechanical strength of the alloy electrodes. Meanwhile, the homogenization of composition can eliminate the lattice stress and the lattice distortion, which enhances anti-pulverization capacity of the alloy electrodes. The analyzed result of the EDS shows that the element content is almost consistent with the actual content.

3.3 Electrochemical Properties

3.3.1 Pressure–Concentration–Temperature Isotherms

Figure 4 illustrates the pressure–concentration–temperature isotherms of the alloys with different melt-spun speeds. It can be found that the maximum hydrogen storage capacity of the melt-spun treatment alloys decreases, especially the melt-spun alloy electrodes (20, 25 m/s). The cell volume of CeCu_5 -type phase decreases, leading to the decrease in hydrogen storage space. Meanwhile the A_5B_{19} -type phase has a better capacity of hydrogen storage than AB_5 -type phase [29]. Thus, the decrease in the maximum storage capacity is mainly related to the decrease in the CeCu_5 -type phase cell volume and the decrease in the $\text{Pr}_5\text{Co}_{19}$ -type phase abundance. It also can be found that melt-spun treatment can improve hydrogen desorption plateau pressure. The improvement in the hydrogen desorption plateau

Table 1 Phase composition and lattice parameters of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys

Samples	Phase	Space group	Phase abundance (%)	Lattice constants (nm)		Cell volume ($\times 10^{-3} \text{ nm}^3$)
				<i>a</i>	<i>c</i>	
As-cast	LaNi_5	P6/mmm (191)	47.9	5.0419	4.0091	88.149
	$\text{Pr}_5\text{Co}_{19}$	R-3 m (166)	30.0	5.0391	32.3712	711.638
	LaNi_2	Fd-3 m (227)	22.1	7.2278	7.2278	377.677
10 m/s	LaNi_5	P6/mmm (191)	51.8	5.0352	3.9907	87.639
	$\text{Pr}_5\text{Co}_{19}$	R-3 m (166)	27.9	5.0375	32.5348	715.362
	LaNi_2	Fd-3 m (227)	20.3	7.2319	7.2319	378.934
15 m/s	LaNi_5	P6/mmm (191)	56.2	5.0308	4.0023	87.743
	$\text{Pr}_5\text{Co}_{19}$	R-3 m (166)	26.0	5.0353	32.5316	714.503
	LaNi_2	Fd-3 m (227)	17.8	7.1812	7.1812	370.331
20 m/s	LaNi_5	P6/mmm (191)	60.9	5.0167	3.9803	86.779
	$\text{Pr}_5\text{Co}_{19}$	R-3 m (166)	18.3	5.0423	32.4677	715.023
	LaNi_2	Fd-3 m (227)	20.8	7.1949	7.1949	372.543
25 m/s	LaNi_5	P6/mmm (191)	62.8	5.0261	4.0003	87.523
	$\text{Pr}_5\text{Co}_{19}$	R-3 m (166)	14.3	5.0538	32.3888	716.549
	LaNi_2	Fd-3 m (227)	22.9	7.1938	7.1938	372.434

Fig. 3 Typical SEM-EDS analysis of the $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys; **a** as-cast; **b** 10 m/s

Fig. 4 Pressure–concentration–temperature curves of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy electrodes

pressure is closely related to the homogenization of alloy composition.

3.3.2 Activation Performance and Maximum Discharge Capacity

Table 2 lists the electrochemical performance parameters of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys. It can be seen that the alloy electrodes can be activated within 2–4 cycles, and with the increase in the melt-spun speed, the $C_{\max}$ of the alloy decreases from $328.09 \text{ mA h g}^{-1}$ (as-cast) to $291.43 \text{ mA h g}^{-1}$ (25 m/s). The increase in the melt-spun speed has a little influence on the activation property, but has negatively effect on the $C_{\max}$ of the alloy electrode. The change result of $C_{\max}$ value and activation performance of the alloy is consistent with the change trend of hydrogen storage capacity.

Table 2 Electrochemical properties of La₄MgNi_{17.5}Mn_{1.5} alloys

Samples	$C_{\max}$ (mA h g ⁻¹)	N_a	HRD (%)			R (Ω)	I_0 (mA g ⁻¹)	D ($\times 10^{-10}$ cm ² s ⁻¹)
			HRD ₃₀₀	HRD ₆₀₀	HRD ₉₀₀			
As-cast	328.09	2	96.89	89.41	85.61	0.36	199.69	1.331
10 m/s	329.01	2	97.73	92.28	86.98	0.36	196.82	1.388
15 m/s	314.27	3	97.42	90.96	85.92	0.42	180.15	1.209
20 m/s	291.56	3	88.10	67.97	50.00	0.94	140.46	1.092
25 m/s	291.43	4	88.00	65.00	49.50	0.97	138.31	1.023

3.3.3 Cyclic Stability

Figure 5 shows the cycle stability curve of the La₄MgNi_{17.5}Mn_{1.5} alloy electrode after melt-spun treatment. As can be seen in Fig. 5, the melt-spun treatment can greatly improve the cycle stability of the alloy electrode. It is known that the larger the capacity retention rate, the better the cycle stability of the alloy [23]. In order to accurately appraise the cycle stability of the alloy electrodes, the capacity retention rates of the as-cast and melt-spun alloys are plotted in Fig. 6. It is observed that the capacity retention rate of the melt-spun alloy is markedly higher than that of the as-cast alloy. For example, the capacity retention rate (S_{100}) of the alloy (25 m/s) is 82.29%, which is higher than 54.82% (as-cast). After 200 cycles, the capacity retention rate (S_{200}) of the alloy (25 m/s) is above 63%. Liu et al. [5] reported that the best capacity retention rate (S_{100}) of the La₄MgNi₁₉, which was synthesized by stepwise sintering LaMgNi₄ and LaNi₅ precursor powders, is 85.7%. Melt-spun treatment also can obtain reasonable result. As a result of the expansion and contraction of the cell volume of the alloy during the process of charge/discharge, the alloy electrode is easy to be pulverized and corroded, and

Fig. 5 Cycle stability curves of La₄MgNi_{17.5}Mn_{1.5} alloy electrode **Fig. 6** Capacity retention rate curves of La₄MgNi_{17.5}Mn_{1.5} alloys after 100 cycles and 200 cycles

the electrode capacity decreases [19]. Melt-spun treatment can improve the anti-pulverization capacity of the alloy, which is helpful to the cycle stability.

3.4 Dynamic Performance

Table 2 shows that with the increase in the melt-spun speed, the change in HRD firstly increases and then decreases. It is known that the HRD of MH electrode is a kinetic performance of hydrogen absorption/desorption of the alloy electrode, mainly depending on the electrochemical reaction rate on the alloy electrode surface and the diffusion rate of hydrogen in the alloy electrode [30, 31]. In order to investigate the mechanism of the hydrogen absorption kinetics of the alloy electrodes, the linear polarization, alternating current impedance and constant potential step were measured. The detailed calculate formula of the I_0 and hydrogen diffusion coefficient (D) can be seen in Ref. [32]. The results are listed in Table 2.

Figure 7 shows the linear polarization curves of La₄MgNi_{17.5}Mn_{1.5} alloy electrodes at 50% DOD (depth of discharge). Table 2 and Fig. 7 show that with the increase

Fig. 7 Linear polarization curves of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy electrode

in melt-spun speed, I_0 of the alloy electrodes decreases while D firstly increases and then decreases. Compared the HRD with the values of I_0 and D , it is found that the variations of D are consistent with the HRD values of the alloy electrodes. It means the HRD of the alloy electrodes is mainly related to the hydrogen diffusion coefficient in the bulk of the alloy.

The electrochemical impedance spectra of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy electrodes at 50% DOD are shown in Fig. 8. All electrochemical impedance spectra of alloy electrodes consist of three parts: a smaller semicircle, a bigger semicircle and an oblique line. According to the study of Kuriyama *et al.* [33], the smaller semicircle at high-frequency region is ascribed to the contact resistance between the alloy powder and the conductive materials, and the larger semicircle in the mid-low-frequency region is ascribed to the charge transfer resistance on the alloy

Fig. 8 Electrochemical impedance spectra of $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy electrodes at 50% DOD

surface. And the oblique line in the lower-frequency region is indicative of hydrogen diffusion in the alloy electrode. Figure 8 shows that the contact resistance almost remains unchanged for the alloy electrodes, while the change transfer resistance is very different, especially when the melt-spun speed is higher than 15 m/s. This means that the electrochemical reaction of the alloy electrode surface becomes difficult with the increase in the melt-spun speed. The change regulation of the charge transfer resistance is consistent with that of the exchange current density. For example, the I_0 value of the as-cast alloy is 199.69 mA g^{-1} , corresponding to the small impedance. The value of the alloy (25 m/s) is 138.31 mA g^{-1} , corresponding to the large impedance. This result conforms with the research result of Ouyang *et al.* [9].

4 Conclusions

(1) The structure analysis reveals that $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloys were composed of CaCu_5 -type phase, $\text{Pr}_5\text{Co}_{19}$ -type phase, CeNi_2 -type phase. With the increase in melt-spun speed, the phase abundance of CaCu_5 -type increases gradually from 48.2% (as-cast) to 63.1% (25 m/s), and that of $\text{Pr}_5\text{Co}_{19}$ -type in the alloy decreases. Melt-spun treatment results in the grain refinement and homogenization of the alloy without changing constituents of the alloy.

(2) The electrochemical measurement shows that all the alloy electrodes have better activation performance within four cycles. Melt-spun treatment can improve the alloy anti-pulverization capacity, which is helpful to the cycle stability. After 100 cycles, the capacity retention rate (S_{100}) of the alloy electrode increased from 54.82% (as-cast) to 82.29% (25 m/s). Even though 200 cycles, the capacity retention rate (S_{200}) of the alloy (25 m/s) is above 63%. However, the C_{max} of the alloy decreases from $328.09 \text{ mA h g}^{-1}$ (as-cast) to $291.43 \text{ mA h g}^{-1}$ (25 m/s).

(3) Through the study of linear polarization, alternating current impedance and constant potential step, it can be learned that melt-spun treatment can decrease the electrocatalytic activity and the hydrogen diffusion rate of the alloy, which leads to the reduction in HRD of the alloy.

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