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Structural phase transformation and electrochemical features of La–Mg–Ni-based AB_4-type alloys

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ABSTRACT

In this work, we studied the structural phase transformation and electrochemical characteristics of AB_4-type La–Mg–Ni-based alloys through zoning annealing of $La_{0.78}Mg_{0.22}Ni_{3.90}$ polymorphic alloy. The as-cast $La_{0.78}Mg_{0.22}Ni_{3.90}$ alloy contained two phases of $LaNi_5$ (50.8 wt.%) and $(La,Mg)_2Ni_7$ (49.2 wt.%). When annealed at 1173 K, solid $LaNi_5$ phase reacted with a liquid phase from $(La,Mg)_2Ni_7$ converting into the $(La,Mg)_5Ni_{19}$ phase. Increasing temperature to 1223 K, the residual $LaNi_5$ phase continued to react with a liquid phase from $(La,Mg)_5Ni_{19}$ forming a new $(La,Mg)_6Ni_{24}$ phase in the alloy. Field-emission scanning electron microscope (FE-SEM) analysis found that the $(La,Mg)_6Ni_{24}$ phase showed diffuse distributing in the alloys and this particular morphology provided plenty of phase boundaries which offered more hydrogen diffusion routes. The high rate dischargeability (*HRD*) of the alloy electrodes increased with higher $(La,Mg)_6Ni_{24}$ phase abundance. When the abundance of $(La,Mg)_6Ni_{24}$ phase raised to 62.0 wt.%, the *HRD* of the alloy electrode at a discharge current density of 1500 mA g^{-1} (HRD_{1500}) reached 68.0%. Meanwhile, the surface exchange current density (I_0) and hydrogen diffusion coefficient (D) increased to 360.35 mA g^{-1} and 2.450×10^{-11} cm^2 s^{-1}, respectively.

1. Introduction

As a kind of promising negative electrode material of nickel-metal hydride (Ni-MH) batteries, La–Mg–Ni-based hydrogen storage alloys have many advantages over the current commercial AB_5-type alloys, such as high discharge capacity and good activation features, etc. [1–4]. However, they are subject to poor cycling stability and low rate dischargeability, which are hampering their practical applications. Accordingly studies regarding improving the cycling stability and rate dischargeability of La–Mg–Ni-based alloys have been considerably performed [5–8]. Studies show that controlling and adjusting the phase structure is an effective way to improve the electrochemical performance of La–Mg–Ni-based alloys [9–11].

La–Mg–Ni-based alloys have super-lattice structures described by stacking along c axis of $CaCu_5$-type [$LaNi_5$] and Laves-type [$LaMgNi_4$] subunits in 1:1, 2:1, 3:1 or 4:1 ratios forming AB_3-type, A_2B_7-type, A_5B_{19}-type or AB_4-type phases, respectively. These phases have close compositions and formation temperatures. Finding out the formation mechanisms of these different phases in La–Mg–Ni system is meaningful but also hard. There are already some researches making contributions to it. Zhang et al. [12] investigated the phase stability, structural transition of the La_4MgNi_{19} compounds by a two-step annealing method and found that the La_4MgNi_{19} phase is stable between 840 °C and 960 °C. Our group [13,14] put forward that at the process of powder sintering, the phase transition between different type phase structures occurred through a series of peritectic reaction starting from $LaNi_5$ and $LaMgNi_4$ powders. It can be concisely expressed as follows:

$$LaNi_5 + LaMgNi_4 \rightarrow (La,Mg)Ni_3 \quad (1)$$

$$LaNi_5 + (La,Mg)Ni_3 \rightarrow (La,Mg)_2Ni_7 \quad (2)$$

$$LaNi_5 + (La,Mg)_2Ni_7(\text{liquid phase}) \rightarrow (La,Mg)_5Ni_{19} \quad (3)$$

In other study the reaction of equation (4) is also reported. Tian et al. [15] proved that $(La,Mg)Ni_3$ phase converted into $(La,Mg)_2Ni_7$

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Table 1
Chemical compositions of the alloys obtained by ICP.

Alloys	La (wt.%)	Mg (wt.%)	Ni (wt.%)	Chemical composition
Design	31.62	1.56	66.82	$La_{0.78}Mg_{0.22}Ni_{3.90}$
As-cast	31.68	1.56	66.76	$La_{0.78}Mg_{0.22}Ni_{3.89}$
1073 K*24 h	31.73	1.54	66.73	$La_{0.78}Mg_{0.22}Ni_{3.90}$
1173 K*24 h	31.54	1.50	66.96	$La_{0.79}Mg_{0.21}Ni_{3.95}$
1223 K*24 h	31.48	1.46	67.06	$La_{0.79}Mg_{0.21}Ni_{3.99}$
1223 K*48 h	31.45	1.35	67.20	$La_{0.80}Mg_{0.20}Ni_{4.06}$

phase with the existence of $LaNi_5$ phase during annealing milled $La_{0.75}Mg_{0.25}Ni_{3.3}Co_{0.5}$ alloy at 600 °C. Recently, Denys et al. [16] studied the phase-structural transformations of the La_2MgNi_9 alloy and detailedly probed the formation process of La_3MgNi_{14} (3R), La_4MgNi_{19} (2H) and La_4MgNi_{19} (3R) phases during the peritectic reactions by *in situ* neutron powder diffraction.

A comprehensive understanding of the phase transformations of La–Mg–Ni-based alloys with different type phases is essential for alloy preparations. For now, the phase transformation and electrochemical characteristics of AB_3-type, A_2B_7-type or A_5B_{19}-type alloy are investigated maturely and widely, except for AB_4-type alloy. There are only a few studies reporting the finding of the AB_4-type phase. In 2007, Qzaki et al. [17] found the existing of AB_4-type phase in $La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(MnAl)_x$ ($0.1 < x \leq 0.4$) alloys. When $x = 0.2$, the AB_4 phase abundance was dominant, reaching to 50%. Besides, Zhang et al. [18] synthesized $La_{0.85}Mg_{0.15}Ni_{3.8}$ compounds containing the La_5MgNi_{24} phase by spark plasma sintering technique and found La_5MgNi_{24} phase forming at higher temperature than the A_5B_{19} or A_2B_7 one. However there is no research reporting the forming conditions and microstructure of the AB_4-type phase and the relevance between phase structure and electrochemical features of AB_4-type alloy still needs further investigation and systematic elaboration.

Based on these, we chose a $La_{0.78}Mg_{0.22}Ni_{3.90}$ alloy and studied the phase transformation via a zoning annealing treatment method. More importantly, the formation process and microstructure of AB_4-type structure were elucidated. Besides, hydrogen

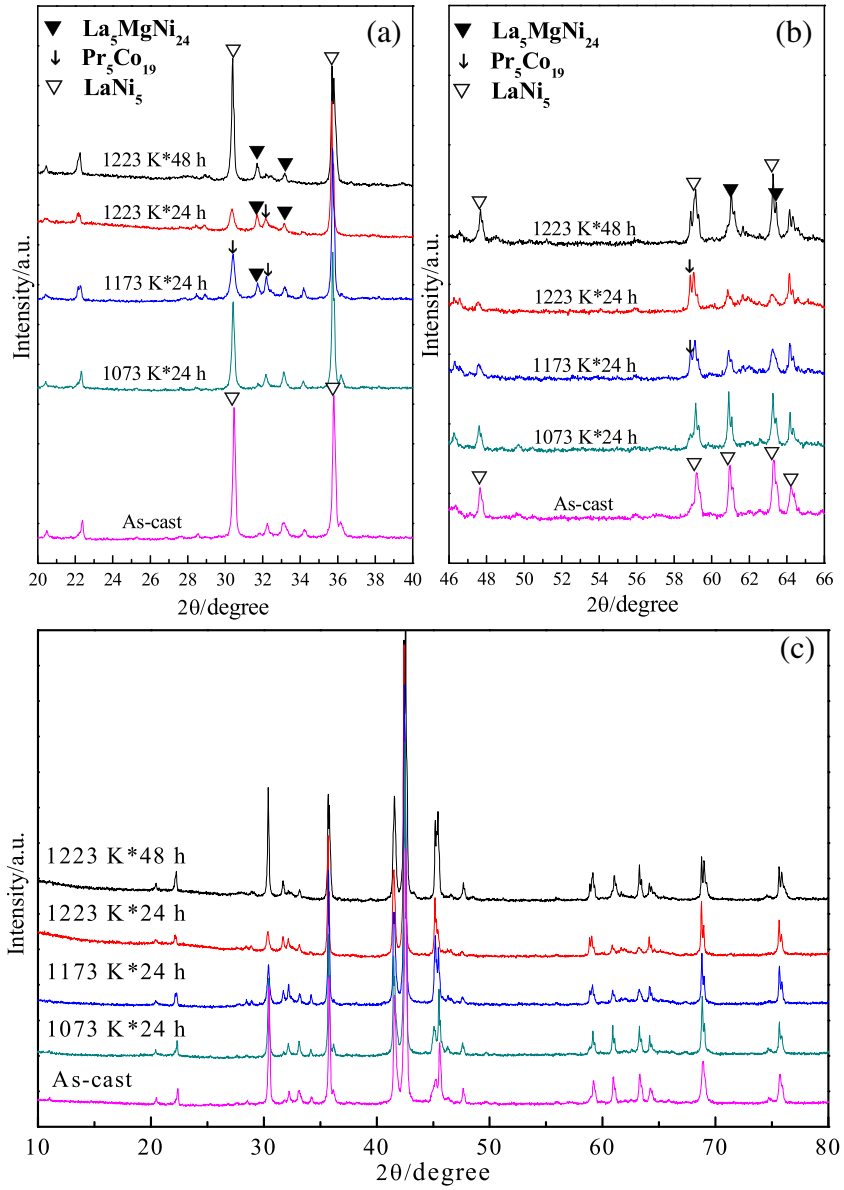

Fig. 1. X-ray diffraction patterns of the alloys in different 2θ ranges: (a) range of 20–40°; (b) range of 46–66°; (c) range of 10–80°.