



Effect of elemental substitution on the structure and hydrogen storage properties of LaMgNi₄ alloy



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ABSTRACT

Intermetallic compounds with the nominal formula LaMgNi_{3.6}M_{0.4} (M = Ni, Co, Mn, Cu, Al) were prepared through induction melting, and the structure and hydrogen storage properties of the resultant alloys were extensively investigated. Results showed that the alloys exhibit sizable hydrogen absorption capacity and that elemental substitution significantly influences their microstructure and hydrogen storage properties. The discharge capacities of the alloy electrodes decrease in the order Co > Ni > Al > Cu > Mn. Moreover, the electrochemical kinetics of the alloys depend on their microstructures and phase compositions. Smaller grain size is helpful to improve the electrochemical kinetics. The gaseous hydrogen absorption capacities of the alloys are approximately 1.7 wt.% in the first hydrogenation process. Cracking caused by hydrogenation and dehydrogenation also significantly improves the hydrogen absorption kinetics of the alloy particles. The hydrogen storage capacities of the alloys rapidly decrease with increasing cycle number. This result is attributed to amorphisation of the LaMgNi₄ phase during hydrogen absorption–desorption cycling (H₂-induced amorphisation). Our findings provide new insights into the capacity degradation mechanism of La–Mg–Ni system hydrogen storage alloys that may improve their cycling stability.

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1. Introduction

As energy shortage and environmental concerns continue to increase, developing and applying new sources of clean and renewable energy has attracted the attention of scientists and engineers all over the world [1,2]. Hybrid electric vehicle (HEV) is an attractive strategy to reduce both energy consumption and CO₂ emissions, considering that a quarter of the world's total energy is consumed by the transportation industry. Approximately 23% of the global CO₂ emission originates from vehicular emissions resulting from the combustion of fossil fuels [3–5]. In 2009, the Ministry of Industry and Information Technology of China enacted 'The regulation of access of new energy automobile production enterprises and products', where HEVs equipped with nickel-metal hydride batteries as an auxiliary power source were classified as a mature product for nationwide selling. This regulation marks the golden age for the development of Ni–MH batteries. Whether hybrid cars can be successfully applied to the global market depends on the electrochemical performance, especially specific capacity, of Ni–MH batteries. The AB₅ family of intermetallic compounds has been

widely used in these batteries because of their good hydrogen absorption–desorption kinetics and suitable thermodynamic performance. However, the hydrogen storage capacity of these hydrides is too low (only approximately 1.3 wt.% or 320 mA h/g) to meet the requirements of power batteries [6,7]. Hence, developing new hydrogen storage materials with higher capacity is necessary to enable the practical applications of Ni–MH batteries in HEVs.

Kohno et al. [8] first reported the hydrogen storage characteristics of La–Mg–Ni system alloys and found that these alloy electrodes exhibit a large discharge capacity (410 mA h/g). Since then, lots of RE–Mg–Ni-based (RE = La, Ce, Pr, Nd, Sm, Y) alloys have been developed as negative electrode materials for Ni–MH batteries [9–11]. Aono et al. [12] synthesised a new intermetallic compound YMgNi₄ through mechanical milling and casting. The reversible hydrogen capacity of YMgNi₄ is approximately 1.05 wt.% under a hydrogen pressure of 4.0 MPa at 313 K. Kadir et al. [13] and Wang et al. [14] also prepared AMgNi₄ (where A = Ca, La, Ce, Pr, Nd, Y) alloys through solid-state sintering technology and systematically investigated their structural and crystallographic characteristics. Amongst the alloys they developed, LaMgNi₄ exhibited great potential for application in hydrogen energy systems. Moreover, the addition of transition metals and other elements may enhance the overall performance of La–Mg–Ni-based hydrogen storage alloys [15–17]. Substitution of Ni by other metals offers the best compromise between high hydrogen storage capacity and good cycle stability [18].

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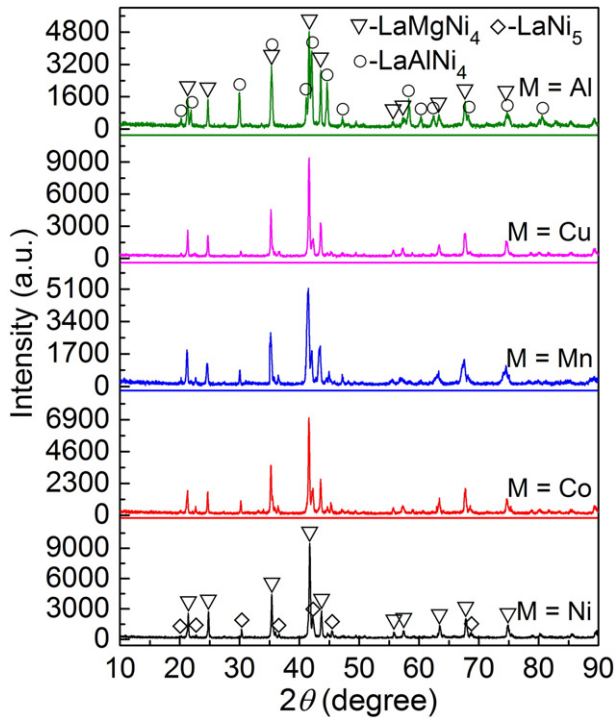


Fig. 1. XRD patterns of the $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloys.

However, the effect of elemental substitution on the hydrogen storage properties of La–Mg–Ni-based AB_2 -type alloy remains unknown.

In the present study, $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloys were prepared through vacuum induction melting. The influence of partial substitution of Ni with Co, Mn, Cu and Al on the phase structure and gaseous and electrochemical hydrogen storage capacities were extensively investigated.

2. Experimental

Elemental La, Mg, Ni, Co, Mn, Cu and Al were used as raw materials to prepare $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloys using the vacuum induction melting method. For convenience, the LaMgNi_4 alloy was denoted as $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni}$) alloy. The component metals were of over 99.5% purity in all cases. Based on our experience, excess Mg (10%) and La (5%) are necessary to compensate for evaporative loss under the present preparation conditions. Alloy melting and casting were performed in a pure helium-protected atmosphere. After stirring for 10 min at approximately 1773 K, the molten alloys were cast into a mould and cooled to room temperature. The alloy ingots were then mechanically crushed into fine powders of lower than 200 mesh for the hydrogen storage performance tests.

X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation was performed in a Rigaku (D/Max-2400) diffractometer to determine the phase structure

and compositions of the alloys. The scanning rate was $2^\circ/\text{min}$, and scanning ranged from 10° to 90° with a step size of 0.02° . 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 micromorphology of the alloy powders before and after hydrogenation was determined using SEM.

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. Carbonyl nickel powder served as the frame of the pellet and current collector. Galvanostatic charge–discharge tests were performed at 303 K in a standard three-electrode open cell comprising a working electrode (alloy electrode), a sintered $\text{Ni}(\text{OH})_2/\text{NiOOH}$ counter electrode with a large excess capacity and a HgO/Hg reference electrode immersed in 6 mol/L KOH electrolyte. Each electrode was charged at 60 mA/g for 8 h and then discharged at the same current density to a cut-off cell voltage of 0.5 V (vs. $-\text{HgO}/\text{Hg}$) after a 10 minute rest. The discharge capacities of the alloys at different discharge current densities (60, 300, 600, 900 and 1200 mA h/g) were also measured to investigate their high-rate dischargeability (HRD).

The gaseous hydrogen storage properties of the alloy powders were measured using a Sievert's-type apparatus (Beijing General Research Institute for Nonferrous Metals, China). The volume of the reactor chamber was held constant at approximately 50 mL. Approximately 1 g of alloy powders was placed into the reactor. The system was first evacuated below 10^{-2} Pa using a vacuum pump, after which the sample was heated up to 323 K and an initial hydrogen pressure of 3 MPa was applied to induce hydrogen absorption of the alloy particles. The experimental hydrogen was of over 99.999% purity.

3. Results and discussion

3.1. Crystal structure characteristics

Fig. 1 shows the XRD patterns of the $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloys. The major phase of all of the alloys is LaMgNi_4 with the $F\bar{4}3m$ (216) space group. For $M = \text{Ni, Co, Mn, Cu}$ alloys, the secondary phase is LaNi_5 with the $P6/mmm$ (191) space group. Addition of Co, Mn and Cu does not produce any significant change in phase composition. By contrast, the secondary phase of the $M = \text{Al}$ alloy changes into LaAlNi_4 with the $P6/mmm$ (191) space group [19]. Table 1 shows the calculated cell parameters of the LaMgNi_4 and LaNi_5 (or LaAlNi_4 for the $M = \text{Al}$) phases as revealed by XRD. Partial substitution of Ni with Co, Mn, Cu and Al obviously increases the lattice parameters of the alloys; this phenomenon is considered to be associated with lattice expansion and distortion resulting from element substitution [20].

Fig. 2 shows SEM images of the as-cast $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloy ingots. All of the alloys clearly display a lamellar structure and two main constituents. This observation, along with the XRD

Table 1

Lattice parameters, cell volumes of the LaMgNi_4 and LaNi_5 (or LaAlNi_4) phases and M/Ni atomic ratios of the $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M = \text{Ni, Co, Mn, Cu, Al}$) alloys.

Alloys	LaMgNi_4 phase			LaNi_5 (or LaAlNi_4) phase			
	a (Å)	V (Å ³)	M/Ni (%)	a (Å)	c (Å)	V (Å ³)	M/Ni (%)
$M = \text{Ni}$	7.176	369.5	100	5.001	4.002	86.68	100
$M = \text{Co}$	7.190	371.2	9.6	5.015	4.009	87.32	13.2
$M = \text{Mn}$	7.204	373.9	9.8	5.027	4.011	87.78	12.8
$M = \text{Cu}$	7.196	372.6	9.2	5.024	4.008	87.61	13.6
$M = \text{Al}$	7.191	371.9	2.6	5.066 (LaAlNi_4)	4.070 (LaAlNi_4)	90.46 (LaAlNi_4)	19.3

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