

# Structures and Hydrogen Storage Properties of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$ ( $x=0.0, 0.1, 0.2, 0.3$ ) Alloys



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**Abstract:**  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  ( $x=0.0, 0.1, 0.2, 0.3$ ) hydrogen storage alloys were prepared by a three-step induction melting. Their crystal structures and hydrogen storage properties were investigated. Results show that alloys with  $x=0.0$  and  $0.1$  contain a single  $\text{LaNi}_4\text{Al}$  phase; however, those with  $x=0.2$  and  $0.3$  are composed of  $\text{LaNi}_4\text{Al}$ ,  $(\text{La}, \text{Mg})\text{Ni}_3$  and  $\text{AlNi}_3$  phases. With  $x$  increasing from  $0.2$  to  $0.3$ , the abundances of the secondary phases and the plateau pressures in the pressure-composition isotherms are lifted significantly. Meanwhile, their hydrogen storage capacities are remarkably reduced. It is found that the alloy with  $x=0.1$  possesses the fastest absorption kinetics compared to the others as well as a good hydrogen capacity and a low plateau pressure.

**Key words:** RE hydrogen storage alloy; Mg substitution; hydrogen storage property

The importance of hydrogen as a clean energy carrier is being widely accepted during recent years, since more and more people recognize that the combustions of fossil fuels would produce such greenhouse gases as oxides of carbon, nitrogen, sulphur, etc.<sup>[1]</sup> which are harmful to the environments and economies. Hydrogen is considered as a potentially non-carbon-based and alternatively eco-friendly fuel, which can be generated from clean and renewable sources<sup>[2]</sup>.

For the coming hydrogen economy society, efficient hydrogen storage and delivery are fundamentally important.  $\text{AB}_3$ -type alloys are preferably used for hydrogen storage. They can reversibly uptake/release hydrogen in ambient conditions. Element substitution has been frequently adopted to improve the ab/de-sorption properties of such alloys<sup>[3-6]</sup>. As a favorable material,  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  is used in storing tritium in such facilities as the Savannah River Site (SRS) of USA<sup>[7]</sup>. Since it is liable to be activated, a delivery pressure higher than 200 kPa can be easily achieved by a moderate heating and nearly entire  $^3\text{H}$  can be captured. So far,  $\text{LaNi}_{4.25}\text{Al}_{0.75}$

alloy as the tritium storage medium has been employed for more than 20 years<sup>[8]</sup>. Cheng et al.<sup>[9]</sup> found that the hydrogen absorption kinetics of the unannealed melt-spun (UMS)  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  alloy was improved from that of annealed induction-melt (AIM) one after 1500 cycles. Furthermore, the utilization of melt-spinning technique resulted in a decreased hysteresis of pressure-composition (P-C) isotherms and an improved pulverization resistance.

In recent years, Mg and Mg-Ni-based alloys have been adopted for on-board hydrogen storage materials because of their high capacity<sup>[10,11]</sup>. In addition, Mg-based hydrides possess some excellent properties such as recyclability, reversibility and heat-resistance<sup>[12]</sup>. Hence, partial substitution of La by Mg in  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  alloy was expected to improve the ab/de-sorption properties. Moreover, the substitution would decrease the cost of the product because Mg is much cheaper than La. However, little attention was paid on the substitution of La by Mg in  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  alloy at present. Therefore, we would focus on the crystal structures and the

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hydrogen storage properties of  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  ( $x=0.0, 0.1, 0.2, 0.3$ ) alloys.

## 1 Experiment

The  $\text{La}_{(1-x)}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  alloys were prepared by electromagnetic induction melting the mixtures of La (99.50%), Ni (99.90%), Al (99.99%) and Mg (99.95%) ingots, using the furnace with a cold crucible under argon atmosphere in the Metallurgical Laboratory of Shanghai University. Because the saturated vapor pressure of magnesium is remarkably high, a three-step melting process was adopted to reduce the loss of Mg. Firstly,  $\text{La}_{1-x}\text{Ni}_{4.25}\text{Al}_{0.75}$  alloy was prepared with Al, La and Ni ingots which were placed in crucible from bottom to top. After the preparation, the as-cast ingot of  $\text{La}_{1-x}\text{Ni}_{4.25}\text{Al}_{0.75}$  alloy was mechanically pulverized. Secondly, Mg was plunged into the bottom of crucible and covered with  $\text{La}_{1-x}\text{Ni}_{4.25}\text{Al}_{0.75}$  pieces to produce  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  alloy. Afterward, the as-cast  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  alloy was crushed into pieces and melted again under the same conditions in order to obtain a homogeneous alloy. At last, the as-cast ingots were sealed in quartz tubes under argon atmosphere for annealing. The annealing was conducted in a muffle furnace at 1173 K for 4 h. After that, the samples were slowly cooled down to room temperature. Since magnesium might lose mass by nearly 15% during the whole process as above mentioned, an excessive Mg of 15% was added to compensate the loss.

The chemical composition of the alloys was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO ARCOS SOP type, Germany). About 200 mg powder with uniform composition was weighed for ICP-OES analysis. Three parallel samples were analyzed for each alloy to ensure reproducibility.

The crystal structures of the alloys were determined by an X-ray diffractometer (XRD, Bruker, D8 ADVANCE type, Germany). The X-ray diffractometer worked with the X-ray of Cu  $K\alpha$  and scanned in the  $2\theta$  range from  $10^\circ$  to  $90^\circ$  at room temperature. The scanning step size and dwell times per step were  $0.02^\circ$  and 0.15 s, respectively. For the XRD analysis, the alloy samples were mechanically crushed and ground into powders. The Rietveld refinements on the XRD pattern were applied to determine the phase abundances and lattice parameters by the TOPAS software (Bruker).

The hydrogen absorption/desorption  $P$ - $C$  isotherms of the alloys were measured on a Sieverts apparatus<sup>[13]</sup> with 99.999% purity hydrogen gas at New Energy Material & Technology Laboratory of Yangzhou University. The samples of about 1g were put into the reaction chamber, evacuated at 373 K for 30 min, and then reacted with 9 MPa hydrogen. After 10 absorption-desorption cycles, the alloys were fully activated. Subsequently, the  $P$ - $C$  isotherms of the hydrogen absorption/desorption and the hydrogen absorption kinetics curves were measured at 363, 383 and 403 K. In the present

paper,  $t_{0.9}$  represents the time taken for absorbing 90% of the maximum hydrogen capacity of an alloy. The slope factor  $S_f$  was defined as:

$$S_f = \lg \frac{P_{\text{wt}\% = 0.8}}{P_{\text{wt}\% = 0.14}} \quad (1)$$

where  $p_{\text{wt}\% = 0.8}$  and  $p_{\text{wt}\% = 0.14}$  are the plateau pressures for a hydrogen storage capacity of 0.8 wt% and 0.14 wt%, respectively.

## 2 Results and Discussion

### 2.1 Alloy phases and crystal structures

The comparison of the ICP-OES results with the designed compositions of  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  alloys in Table 1 reveals that the ICP-OES results agreed well with the designed alloy compositions, with a relative deviation of La, Ni, Al and Mg content of about  $\pm 5\%$  for most of the alloy samples.

The XRD patterns in Fig.1 have characterized three phases in the  $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{4.25}\text{Al}_{0.75}$  ( $x=0.0, 0.1, 0.2, 0.3$ ) alloys, which are  $\text{LaNi}_4\text{Al}$  phase with a  $\text{CaCu}_5$ -type hexagonal structure,  $(\text{La,Mg})\text{Ni}_3$  phase with a  $\text{PuNi}_3$ -type rhombohedral structure and  $\text{AlNi}_3$  phase with an  $\text{AuCu}_3$ -type cubic structure. The  $\text{LaNi}_4\text{Al}$  and the  $(\text{La,Mg})\text{Ni}_3$  are hydrogen absorbable phases, but the  $\text{AlNi}_3$  is not such kind of phase<sup>[14,15]</sup>. The Rietveld method was applied in this study for a quantitative phase analysis. As an example, the Rietveld refinement pattern for the alloy with  $x=0.3$  is exhibited in Fig.2. The patterns calculated using the Rietveld method fit well with the patterns obtained by the XRD analysis. For the Rietveld refinements, the structural models for  $\text{LaNi}_4\text{Al}$ ,  $(\text{La,Mg})\text{Ni}_3$  and  $\text{AlNi}_3$  phases were taken from the reported  $\text{CaCu}_5$ <sup>[16]</sup>,  $\text{PuNi}_3$ <sup>[17]</sup> and  $\text{AuCu}_3$ <sup>[18]</sup> structures, respectively. Crystal structure characterizations and the evolution of phases abundances for the alloys reveal that the phase structures and abundances of the alloys change with Mg content (Table 2, Fig.3). When  $x$  is equal to 0.0 and 0.1,  $\text{LaNi}_4\text{Al}$  is the single phase in the alloys, suggesting that Mg fully dissolves into the alloy with  $x=0.1$ . However, when  $x$  is increased to 0.2 and 0.3, the  $(\text{La,Mg})\text{Ni}_3$  and  $\text{AlNi}_3$  phases appear in the alloys. When  $x$  is increased from 0.2 to 0.3, the abundance of the  $\text{LaNi}_4\text{Al}$  phase drops from 67.3 wt% to 52.8 wt%, whereas the abundances of  $\text{AlNi}_3$  and  $(\text{La,Mg})\text{Ni}_3$  phases increase from 18.30 wt% to 25.63 wt% and 14.35 wt% to 21.51 wt%, respectively. These structural changes most likely affect the ab/de-sorption properties of the alloys.

Table 2 shows the crystallographic parameters of all phases in the alloys, which coincides well with those published in literatures<sup>[14, 19, 20]</sup>. The cell volume of the main phase  $\text{LaNi}_4\text{Al}$  slightly decreases with increasing Mg content. While the cell volume of the  $(\text{La,Mg})\text{Ni}_3$  phase decreases when  $x$  is changed from 0.2 to 0.3. The  $\text{LaNi}_4\text{Al}$  phase has a  $\text{CaCu}_5$ -type hexagonal structure. In the present work, the transfer energy

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