

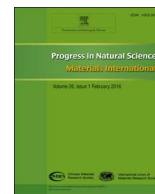
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Review

New approaches for rare earth-magnesium based hydrogen storage alloys[☆]Huawei Zhang^a, Xinyao Zheng^a, Xiao Tian^b, Yang Liu^{c,*}, Xingguo Li^{a,*}^a College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China^b College of physics and electronic information, Inner Mongolia Normal University, Huhehaote 010022, China^c Department of Food Science, Beijing Union University, Beijing 100101 China

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ABSTRACT

As the most possibility applied to the next generation negative electrode materials of Ni/ MH second battery, rare earth (RE)-magnesium (Mg) based alloys have been developed over the last few years. Recent advances about the RE-Mg based intermetallic compounds on the crystal structures, hydrogenation behaviors and electrochemical performances are reviewed in the paper. On the other hand, new results about the preparation and modification methods of the alloys are also covered in details.

1. Introduction

At the modern times, the development and utilization of new clean energy has become an extremely important issue along with environment worsening and fossil fuel, such as oil and natural gas, drying up. Hydrogen is a new kindly energy, highly abundant and non toxic renewable. The most commonly used method for hydrogen storage and its capacities were exhibited in Fig. 1 [1].

Since the AB₅-type alloys were used in Ni/MH batteries as electrode the higher capacity hydrogen storage alloys are concerned more and more. Mg-containing rare earth-based superlattice MH alloys with higher storage capacity, lower self-discharge, and extended cycle stability have attracted a lot of attentions as the replacements for conventional AB₅ alloys [2–4]. Metal or alloys hydride thermodynamics are usually measured by pressure-composition-temperature (PCT) curves, and the reaction enthalpy (ΔH) and entropy (ΔS) could be obtained through fitting the PCT data with van't Hoff equation. The ideal decomposition enthalpy of hydrogen storage alloys which could be applied in Ni/MH batteries was 39–40 kJ mol⁻¹H₂ (H₂ pressure of 1–10 bar at 353 K).

As we all know, one interest point for the RE-Mg based alloys is its crystal feature as it relates to the storage and release of hydrogen. Some researchers [5,6] pointed out that Mg substitutes La position in the AB_x model, where $x=(5m+4)/(m+2)$, m an integer, and A is La or Mg; B is Ni, which could be described by the stacking along the c axis of [AB₅] and [A₂B₄] units following two possible sequences: R3m rhombohedral symmetry (3R) and the hexagonal P63/mmc space group(2H). This could be used as a gift for designing the RE-Mg based

hydrogen storage alloys.

In this review, the recent research progress with respect to crystal structures, hydrogenation behaviors, electrochemical properties, and the preparation and modification methods have been summarized for the rare earth (RE)-Magnesium (Mg) based intermetallics compound. Therefore, there are great need to investigate the competitiveness from the commonness of the alloy to provide guide and suggestion to the development for the hydrogen storage alloys.

2. Characters, gas-solid reactions and electrochemical properties

2.1. AB₂ type

The AB₂ type hydrogen storage alloys with Laves phases caused more and more attentions for those higher capacities. As early as 1980, Oesterreicher et al. [7] firstly prepared the single-phase alloys with the C15-type (MgCu₂ type) structure of La_{1-x}Mg_xNi₂ alloys by induction melting under argon atmosphere. They also found that the alloy structures would transformed into C36- type (MgNi₂ type) as x is greater than 0.67. Mg-rich La_{1-x}Mg_xNi₂ alloys could form the highly stable hydride at room temperature. So far there are only one type of Mg based AB₂ alloys, REMgNi₄ (where RE= La, Ce, Pr, Nd, Y, Gd and Sm), with the MgCuAl₂ structures [8].

Cheng et al. [9] investigated one LaMgNi₄ compound used first principles density functional theory. The La atoms form an fcc sublattice and occupy the (4a: 0, 0, 0) sites, the Mg atoms and Ni₄ tetrahedra were in the tetrahedral sites (4c: 0.25, 0.25, 0.25) with an

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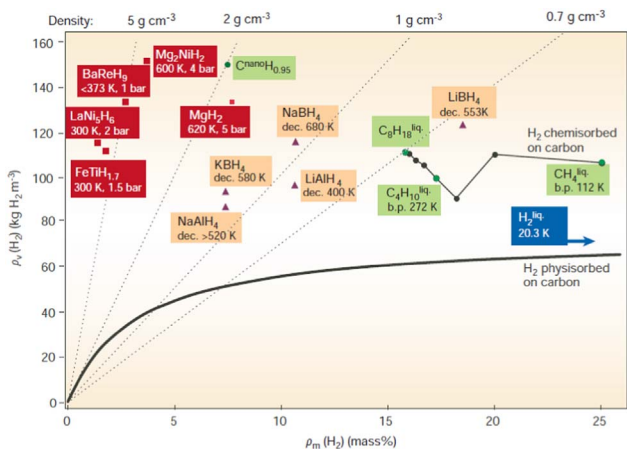


Fig. 1. Stored hydrogen per mass and per volume [1].

ordered way. There are three well-defined hydride structures: α -cubic, β -orthorhombic distorted and γ -cubic symmetry as shown in Fig. 2. Wang et al. [10] studied the electrochemical performances of the REMgNi_4 alloys and the capacities decreased with the order of PrMgNi_4 , CeMgNi_4 , NdMgNi_4 , LaMgNi_4 . The typical PCI curves of LaMgNi_4 at various temperatures (373, 398 and 423 K) are shown in Fig. 5. There are two plateaus at the 373 K, but one at 423 K and the maximum hydrogen content is 1.45%. It is not common to see this phenomenon in other REMgNi_4 compounds [11,12]. Tan et al. [13] prepared the $\text{LaMgNi}_{4-x}\text{Co}_x$ ($x=0, 0.3, 0.5$) compounds by the method of levitation melting. They found that almost the same results would be appeared for the substitution.

Yang et al. [14,15] studied the hydrogen storage properties of $\text{LaMgNi}_{3.6}\text{M}_{0.4}$ ($M=\text{Cu, Mn, Co, Ni}$ and Al). The phase compositions were LaMgNi_4 and LaNi_5 and LaAlNi for $M=\text{Al}$. The maximum hydrogen capacities for these alloys were all about 1.7 wt%, and the cycle stability increased in the following $\text{Mn, Cu, Ni, Co, Al}$.

Otherwise, the microstructure of these hydrogen storage alloys could be altered between polycrystalline and amorphous during a reversible hydrogenation process, especially for AB_2 C15-Laves phase alloys [16,17]. Young et al. [18] investigated the phase transformation

process from polycrystalline to amorphous for LaMgNi_4 alloy, and proved this phenomenon through TEM analysis as shown in Fig. 3.

The electrochemical properties of LaMgM_4 ($M=\text{Co, Mn, Cu, Al}$) with AB_2 -type alloy were studied [15]. With the increasing of the grain size of the alloys the electrochemical kinetics was decreasing usually. The activation capabilities of the $\text{LaMgNi}_{4-x}\text{Co}_x$ alloys were also studied [13]. The alloys could be completely activated after 4 cycles. The discharge capacities could increase from about 250 mAh g^{-1} ($x=0$) to about 300 mAh g^{-1} ($x=0.5$) with the difference of Co content. But there were low cycle stability for all the samples.

2.2. AB_3 type

For the AB_3 type of RE-Mg-based hydrogen storage alloys, the series of REMg_2Ni_9 with PrNi_3 structure (R-3m space group) and REMg_2Cu_9 with CeNi_3 structure (P63/mmc space group) were the most common forms [19–21]. The element substitution type of $(\text{Ca}_{0.5}\text{Y}_{0.5})(\text{CaMg})\text{Ni}_9$ have been particularly studied because of the higher capacity. The alloy structure could be generalized as AB_5 type made by stacking of AB_5 and AB_2 type along the c axis [22].

Chen et al. [23,24] prepared various kinds of RE-Mg-Ni based intermetallics compounds with PuNi_3 structure, such as LaMgCaNi_9 , $\text{LaCaMgNi}_6\text{Al}_3$ and $\text{LaMgCaNi}_6\text{Mn}_3$, et al. Mg atoms are only located at 6c sites while the Ca and La atoms occupy the 6c and 3a sites. The PCT curves of LaMg_2Ni_9 alloy and $(\text{La}_{0.65}\text{Ca}_{0.35})(\text{Mg}_{1.32}\text{Ca}_{0.68})\text{Ni}_9$ were investigated by Kadir et al. [21] at room temperature, 3.3 MPa H_2 pressure. A poor hydrogen absorption/desorption abilities with about 0.33 wt% for the pure LaMg_2Ni_9 alloy were exhibited in the picture. Otherwise, the $(\text{La}_{0.65}\text{Ca}_{0.35})(\text{Mg}_{1.32}\text{Ca}_{0.68})\text{Ni}_9\text{-H}_x$ system obviously contains two phases of $(\text{La}_{0.65}\text{Ca}_{0.35})(\text{Mg}_{1.32}\text{Ca}_{0.68})\text{Ni}_9$ and $(\text{La}_{0.65}\text{Ca}_{0.35})(\text{Mg}_{1.32}\text{Ca}_{0.68})\text{Ni}_9\text{H}_{13}$, respectively, and the hydrogen storage capacity was 1.87 wt% H/M. The research showed that the substitution of La and Mg with Ca could promote the hydrogen storage capacities [20–22].

Yartys et al. [25] have investigated the performances for the $\text{La}_{3-x}\text{Mg}_x\text{Ni}_9$ ($x=0.5, 0.7, 1.0, 1.5$ and 2.0) hydrides. They found that the hydrogen ab/desorption equilibrium pressures of the Mg-rich LaMg_2Ni_9 were much higher than the Mg-poor $\text{La}_{2.3}\text{Mg}_{0.7}\text{Ni}_9$ alloys. Yartys et al. [26] also studied the relationship between the structure

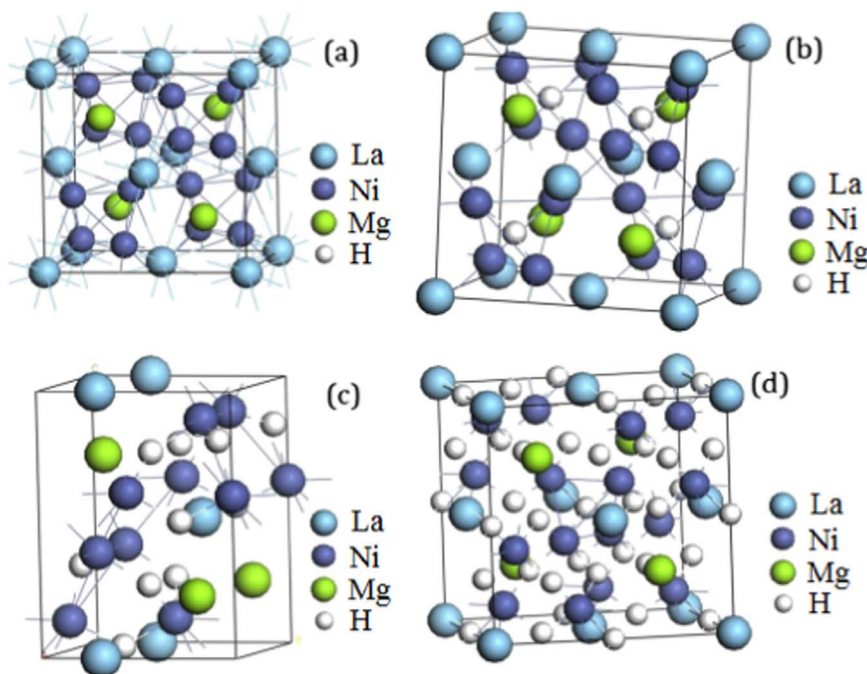


Fig. 2. Structures of LaMgNi_4 compounds (a), α - LaMgNi_4H (b), β - LaMgNi_4H (c) and γ - $\text{LaMgNi}_4\text{H}_7$ (d).

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