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La-H 化合物对 $LaMg_2Ni$ 合金中 Mg_2Ni 相吸氢过程的影响

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摘要：采用感应熔炼技术在 Ar 气氛保护下制备得到 $LaMg_2Ni$ 与 Mg_2Ni 合金。X 射线衍射(XRD)图表明 $LaMg_2Ni$ 合金在吸氢过程中分解为 LaH_3 相和 Mg_2NiH_4 相,放氢过程中 LaH_3 相转化为 La_3H_7 相。与 Mg_2Ni 合金相比,$LaMg_2Ni$ 合金显示出优良的吸氢动力学性能,这是由于镧氢化合物的存在及其在吸氢过程中所发生的相转变所造成的。$LaMg_2Ni$ 合金 280 s 内吸氢即可达到最大储氢量的 90%以上,而 Mg_2Ni 合金则需要 1200 s 才能达到,且在相同温度下 $LaMg_2Ni$ 合金的吸氢反应速率常数大于 Mg_2Ni 合金速率常数。镧氢化合物不仅有利于改善动力学性能,而且可以提高热力学性能。$LaMg_2Ni$ 合金中的 Mg_2Ni 相氢化反应焓与熵分别为−53.02 kJ·mol^{-1} 和 84.96 J·K^{-1}·mol^{-1}(H_2),这一数值小于单相 Mg_2Ni 氢化反应焓与熵(−64.50 kJ·mol^{-1}, −123.10 J·K^{-1}·mol^{-1}(H_2))。压力−组成−温度 (*P-C-T*) 测试结果表明在 603 K 至 523 K 温度范围内,$LaMg_2Ni$ 合金储氢容量保持稳定为 1.95wt%左右，然而 Mg_2Ni 合金的储氢容量则由 4.09wt%衰减为 3.13wt%,Mg_2Ni 合金的储氢容量在 523K 低温下仅为 603 K 时的 76.5%，表明镧氢化合物能够改善 Mg_2Ni 合金低温下的吸放氢性能。

关键词：储氢合金；相转变；镧氢化合物；吸氢动力学
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Effect of La hydride Compound on Hydriding Process of Mg_2Ni Phase in $LaMg_2Ni$ Alloy

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Abstract: $LaMg_2Ni$ and Mg_2Ni alloys were prepared by inductive melting under Ar atmosphere. X-ray diffraction (XRD) shows that during hydrogenation, $LaMg_2Ni$ alloy decomposes to LaH_3 phase and Mg_2NiH_4 phase, in dehydriding process this alloy releases H_2 and LaH_3 phase changes to La_3H_7 phase. Compared with Mg_2Ni alloy, on account of the existence of La hydride compound and phase transition from La_3H_7 phase to LaH_3 phase in hydriding process, $LaMg_2Ni$ alloy shows better hydriding kinetics. It is within 280 s for $LaMg_2Ni$ alloy to reach 90% of the maximum hydrogen absorption capacity, while it needs 1 200 s for pristine Mg_2Ni alloy to do so. The rate constant of $LaMg_2Ni$ alloy is larger than that of Mg_2Ni alloy at the same temperature. La hydride compound is beneficial not only to the enhancement of hydriding kinetics but also to the improvement of the thermodynamic properties. The enthalpy and entropy for the hydriding Mg_2Ni in the $LaMg_2Ni$ alloy are −53.02 kJ·mol^{-1}, 84.96 J·K^{-1}·mol^{-1} (H_2), respectively. Mg_2NiH_4 in $LaMg_2Ni$ alloy is less stable than pristine Mg_2Ni alloy (−64.50 kJ·mol^{-1} and −123.10 J·K^{-1}·mol^{-1} (H_2)). Pressure-Composition- Temperature (*P-C-T*) measurement results show that the hydrogen storage capacity of $LaMg_2Ni$ alloy is about 1.95wt% and is kept stable from 603 K to 523 K, while the hydrogen storage capacity of pristine Mg_2Ni alloy declines distinctly form 4.09wt% to 3.13wt% with the reduction

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of temperature from 603 K to 523 K. The hydrogen storage capacity of pristine Mg_2Ni alloy at lower temperature (523 K) is only 76.5% when compared to that at 603 K, suggesting that La hydride compound could improve the hydriding/dehydriding properties of Mg_2Ni alloy at low temperature.

Key words: hydrogen storage alloy; phase transition; La hydride compound; hydriding kinetic

A great deal of research on hydrogen as an alternative energy source has been carried out during the past decades, many hydrogen storage materials have been discovered for storing and transporting hydrogen safely and economically. Among these materials, Mg has been considered as a promising candidate because of its high hydrogen capacity (up to 7.60wt%), reversibility and low cost [1]. However, its poor kinetic properties during hydrogenation/dehydrogenation (H/D) process and the normally required high dehydrogenation temperature (>573 K), has limited its industrial application.

Until now, there are several approaches to improve the properties of Mg-based alloy. One of the most possible solutions is alloying with transition metal (Ni, Cu and Ti, etc.), such as Mg_2Ni[2-3] alloy, to improve kinetic performances of pure magnesium. A further improvement of absorption/desorption conditions may be obtained by alloying with rare earths, the rare earth hydride corresponding to rare earth element forms in the hydrogen adsorption process, and the rare earth hydride can effectively catalyze hydriding/dehydriding kinetics [4-5]. Other reported methods for the improvement of the Mg based materials hydrogen storage ability include ball milling with catalyst [6-7], surface modification with acid [8] and some new preparing methods for hydrogen storage alloys such as Hydriding Combustion Synthesis (HCS) [9], Spark Plasma Sintering[10] etc.

Recently, many researches[11-12] have focused on $LaMg_2Ni$ compound, an amorphous phase of $LaMg_2Ni$ could be obtained by means of melt spinning technique, hydrogenation at 443 K leads to the formation of $LaMg_2NiH_7$; at higher temperatures (523 K) LaH_x phase and Mg_2NiH_4 phase were produced, but the effect of La hydride compound was not mentioned in $LaMg_2Ni$ alloy [13]. Ouyang et al.[14] found that the actual hydrogen absorption phase was Mg_2Ni phase for the $LaMg_2Ni$ alloy prepared by inductive melting and $LaH_{2.46}$ phase existed in the whole process, the $LaH_{2.46}$ phase was helpful to improve hydriding kinetics of $LaMg_2Ni$ alloy. However, it did not explain in detail how the La hydride compound acted as a catalyst in $LaMg_2Ni$ alloy. Herein we report the hydrogen storage ability of $LaMg_2Ni$ alloy and its phase transition during the hydriding/dehydriding (H/D) process, in particular, effect of La hydride compound on hydriding process of Mg_2Ni phase in $LaMg_2Ni$ alloy.

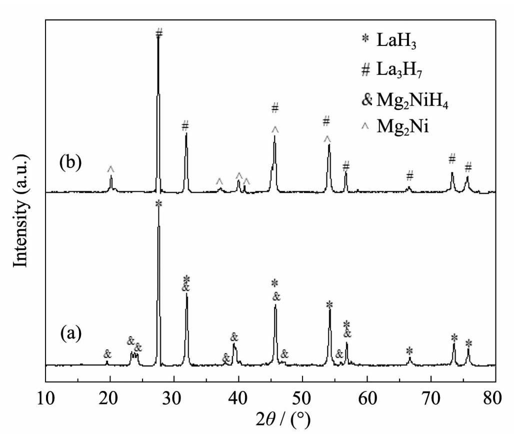
1 Experimental

$LaMg_2Ni$ and Mg_2Ni ingots were prepared by inductive melting of high-purity La, Mg and Ni (purity more than 99.9%) in a magnesia crucible under argon atmosphere. A slight excess of Mg was used to compensate for evaporative Mg loss during the melting procedure[15]. Then the ingots were annealed at 738 K for 6 h. The composition of these alloys was analyzed by Inductive Coupled Plasma Emission Spectrometer (ICP). The phase structures of the as-cast alloy and hydrogenated alloy were measured on a D/max-2500/PC X-ray diffractometer with Cu $K\alpha$ radiation (λ = 0.154 06 nm). The X-ray intensity was measured at 40 kV, 100 mA over a diffraction angle from 10° to 80° with a scan rate of $2^\circ \cdot min^{-1}$. The cell unite volume was calculated by Jade-5 software. The mechanical ball milling experiment was carried out by Pulverisette 6 planetary mono mill made in Germany; ball vs. sample ratio was 15 :1. The hydriding/dehydriding behavior was measured by Pressure-Composition-Temperature (*P-C-T*) characteristic measurement equipment (made by Suzuki Shokan, Japan). The measurement conditions were set as: delay time 300 s, maximum pressure 3.0 MPa. The specimen weight for *P-C-T* measurement is ~ 2.0 g. The hydriding kinetic of the as-cast alloy was also tested by *P-C-T* characte-ristic measurement equipment under the initial hydrogen pressure of 3.0 MPa. The activation conditions could be illustrated as follows, the $LaMg_2Ni$ and Mg_2Ni alloys hydrogenated under 3.0 MPa hydrogen pressure for 2 h, and the dehydriding process was in vacuum for 2 h, the temperature of activation was 623 K.

2 Results and discussion

Fig.1 shows the XRD patterns of $LaMg_2Ni$ alloy after hydriding/dehydriding process. From pattern (a), it reveals that $LaMg_2Ni$ alloy transforms to LaH_3 phase and Mg_2NiH_4 phase after hydriding process at 623 K, while there is no $LaMg_2NiH_7$ phase peak, which is consistent with the results of references [16-17]. The reaction of $LaMg_2Ni$ phase can be summarized as follows:

$$LaMg_2Ni \xrightarrow{\text{Hydrogenation}} LaH_3+Mg_2NiH_4$$



(a) hydrogenation; (b) dehydrogenation

Fig.1 XRD patterns of $LaMg_2Ni$ alloy at 623 K

To understand phase transition during the hydriding/dehydriding (H/D) process more clearly, XRD pattern of $LaMg_2Ni$ alloy after dehydriding process at 623 K was collected and is shown in Fig.1 (pattern (b)). Apparently, after dehydriding process, LaH_3 phase transforms to La_3H_7 phase, while Mg_2Ni phase exists, the reaction can be written as follows:

$$LaH_3+Mg_2NiH_4 \underset{\text{Hydrogenation}}{\overset{\text{Dehydrogenation}}{\rightleftharpoons}} La_3H_7+Mg_2Ni+H_2$$

This phase transition during hydriding/dehydridng process was not found before, we presume that besides the existence of La hydride compound, this phase transition plays an important role in improving hydriding/dehydridng properties of $LaMg_2Ni$ alloy.

For improving hydriding/dehydriding kinetics of $LaMg_2Ni$ and Mg_2Ni alloys, activation is made at 623 K and hydrogen absorption curves are shown in Fig.2 and Fig.3, the initial hydrogen pressure is 3.0 MPa. The as-cast Mg_2Ni alloy can not be activated at 623 K, so activation curves of Mg_2Ni alloy are measured after ball-milling for 2 h. It is clearly seen from Fig.2 that at the first activation cycle, the uptake time for 90% hydrogen content of the maximum hydrogen storage capacity of $LaMg_2Ni$ alloy is 1 560 s, for Mg_2Ni alloy is 1510 s. For the second activation cycle, from Fig.3, the uptake time for 90% hydrogen content of the maximum hydrogen storage capacity of Mg_2Ni alloy is 1200 s, while for $LaMg_2Ni$ alloy, it only needs 280 s. According to XRD analysis, in $LaMg_2Ni$ alloy, it decomposes to La hydride compound and Mg_2NiH_4 during hydriding process, the existence of La hydride compound accelerates hydrogen absorption/desorption rate, because it increases reactive surface area greatly and decreases diffusion length of hydrogen [4,18]. Moreover La hydride compound undergoes phase transition from La_3H_7 phase to LaH_3 phase during hydriding process, the unit cell volume of La_3H_7 phase is 0.357 4 nm^3 with tetragonal La_3H_7 type structure and that of LaH_3 phase is 0.176 1 nm^3 with cubic

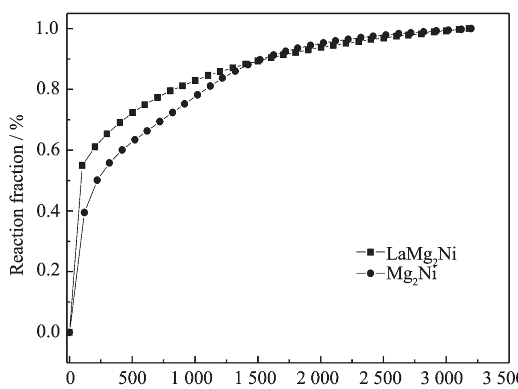


Fig.2 First cycle activation curves of $LaMg_2Ni$ and Mg_2Ni alloys at 623 K

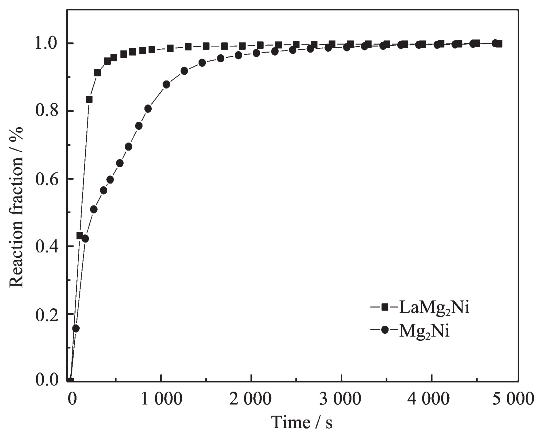


Fig.3 Second cycle activation curves of $LaMg_2Ni$ and Mg_2Ni alloys at 623 K

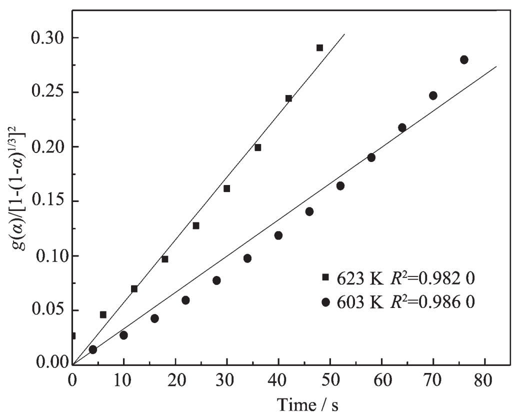


Fig.4 $g(\alpha)$ vs. time for $LaMg_2Ni$ at different temperature

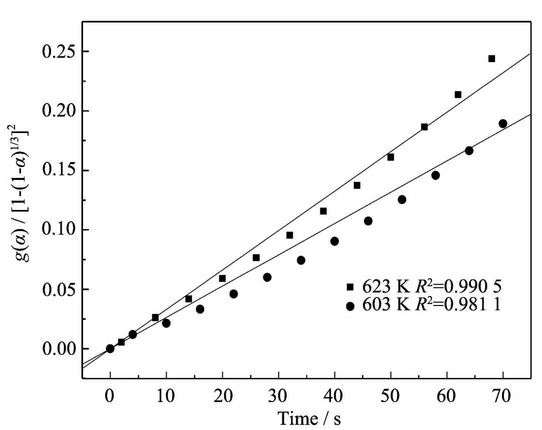


Fig.5 $g(\alpha)$ vs. time for Mg_2Ni at different temperature

CeH_3 type structure. The unite cell volume of La_3H_7 is about two times of LaH_3, although the whole volume of La hydride compound does not change during hydriding process, lattice interface of $LaMg_2Ni$ alloy becomes larger than before, so we believe that the co-catalysis of existence of La hydride compound and this phase transition is beneficial to improve hydriding kinetics of $LaMg_2Ni$ alloy.

The hydrogen absorption process of $LaMg_2Ni$ and Mg_2Ni alloys can be best fitted to Eq. (**1**) (Jander rate equation)

$$g(\alpha) = [1-(1-\alpha)^{1/3}]^2=kt \qquad \text{Eq.(1)}$$

The Eq.(**1**) is rate expression of Jander Diffusion Model (JDM), where α is the reacted fraction vs. time t, k is the rate constant.

The hydrogen absorption process can be described by three-dimensional diffusion mechanism, and the temperature-dependent rate constants (k) are obtained from the slope of each of the straight lines obtained from Fig.4 and Fig.5.

The rate constants of $LaMg_2Ni$ and Mg_2Ni alloys at different temperatures are shown in Table 1. The k value of $LaMg_2Ni$ alloy is larger than that of Mg_2Ni alloy at the same temperature, which indicates that $LaMg_2Ni$ alloy shows better hydriding kinetics than Mg_2Ni alloy. This result is in good agreement with the above analysis about activation for these two alloys.

Hydrogen storage performance of $LaMg_2Ni$ and Mg_2Ni alloys are evaluated by measuring *P-C-T* at different temperatures. Fig.6 and Fig.7 show the *P-C-T* curves of the two alloys measured at 603 K, 573 K and 523 K. It is worth noting that this set of data was collected right after the activation H/D cycle at 623 K and tested in order of the reduction of temperature. As

Table 1 Rate constants of $LaMg_2Ni$ and Mg_2Ni alloys at different temperature

Sample	Temperature / K	k / s^{-1}
$LaMg_2Ni$	623 K	0.005 74
	603 K	0.003 33
Mg_2Ni	623 K	0.003 32
	603K	0.002 63

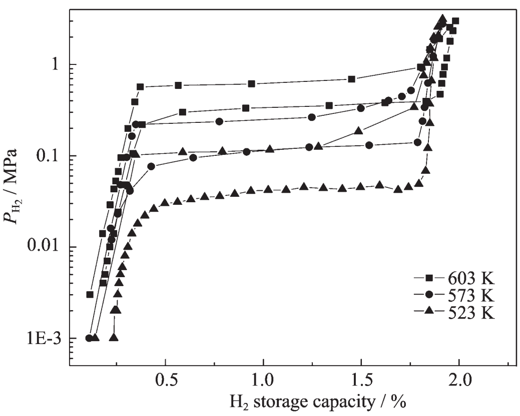


Fig.6　*P-C-T* curves of $LaMg_2Ni$ alloy at different temperatures

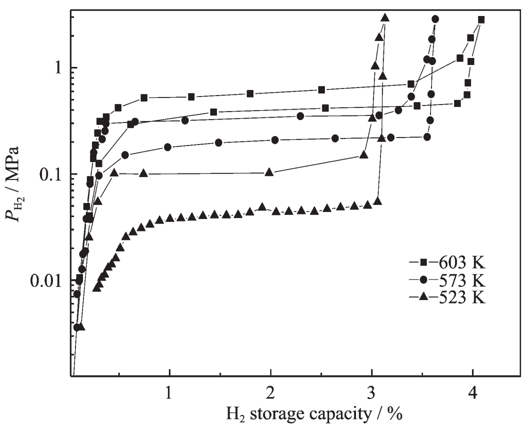


Fig.7　*P-C-T* curves of Mg_2Ni alloy at different temperatures

shown in Fig.6, hydrogen storage capacity of $LaMg_2Ni$ alloy is 1.98wt% (603 K), 1.92wt% (573 K) and 1.91wt% (523 K), respectively. Its hydrogen storage capacity keeps stably with the temperature decreases from 603 K to 523 K. It is clearly seen from Fig.7 that hydrogen storage capacity of Mg_2Ni alloy is 4.09wt% (603 K), 3.63wt% (573 K) and 3.13wt% (523 K), with the reduction of temperature, hydrogen storage capacity of Mg_2Ni alloy declines distinctly. The relative hydrogen storage capacity of $LaMg_2Ni$ and Mg_2Ni alloys vs. temperature is shown in Fig.8. The relative hydrogen storage capacity is defined and calculated by the following equation:

$$S_T = \frac{C_T}{C_{603\ K}} \times 100\% \qquad \text{Eq.}(\mathbf{2})$$

Where S_T is the relative hydrogen storage capacity at T temperature, C_T is the hydrogen storage capacity at T temperature and $C_{603\ K}$ is the hydrogen storage capacity at 603 K.

From Fig.8, it can be seen that the $S_{523\ K}$ of $LaMg_2Ni$ alloy is 96.4%, while that for Mg_2Ni alloy is 76.6%. The hydrogenation plateau of $LaMg_2Ni$ alloy is higher than Mg_2Ni alloy at the same temperature, hydrogenation plateau of pristine Mg_2Ni is 0.56 MPa while that of $LaMg_2Ni$ is 0.74 MPa at 603 K. According to the XRD result of $LaMg_2Ni$ alloy, after H/D process, $LaMg_2Ni$ transforms to La hydride compound and Mg_2Ni, compare with pristine Mg_2Ni alloy, *P-C-T* curves suggest that the La hydride compound is helpful to the improvement of the hydrogen storage property for the Mg_2Ni phase in the $LaMg_2Ni$ alloy at low temperature.

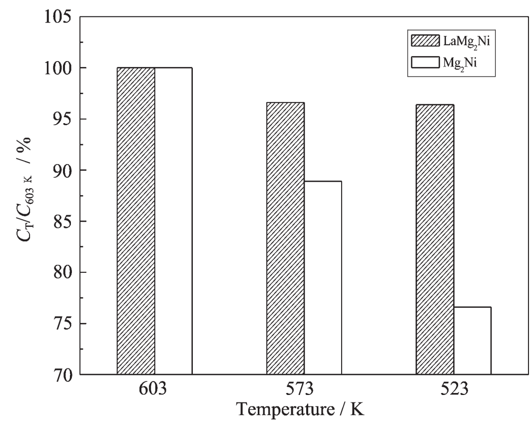


Fig.8　Relative hydrogen storage capacity of $LaMg_2Ni$ and Mg_2Ni alloys vs. temperature

In order to study the thermodynamic property of $LaMg_2Ni$ alloy, *P-C-T* curves of $LaMg_2Ni$ alloy are plotted after the measurement of H/D process at different temperatures, the plateau pressure and temperature are plotted according to the Van′t Hoff equation (Eq. (**3**)). The Van′t Hoff plot for the hydrogenated $LaMg_2Ni$ alloy is shown in Fig.9. The enthalpy and entropy for the hydriding Mg_2Ni in the $LaMg_2Ni$ alloy are calculated to be $-53.02\ kJ\cdot mol^{-1}$, $-84.96\ J\cdot K^{-1}\cdot mol^{-1}$ (H_2). Its hydride is less stable than pristine Mg_2Ni alloy ($-64.50\ kJ\cdot mol^{-1}$ and $-123.10\ J\cdot K^{-1}\cdot mol^{-1}$ (H_2), which shows that La hydride compound is beneficial to reducing the enthalpy and entropy for the hydriding Mg_2Ni in the $LaMg_2Ni$ alloy. $K^{\ominus}$ is the equi-

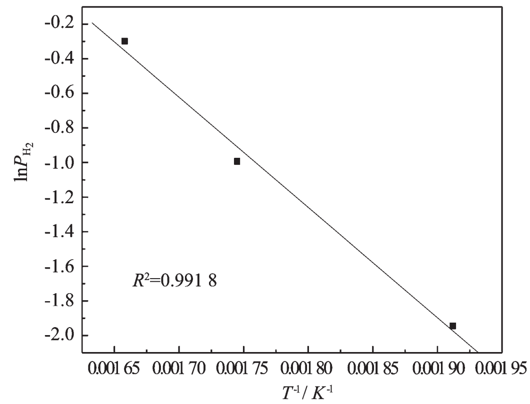


Fig.9 Vant Hoff plot for the hydrogenated $LaMg_2Ni$ alloy

librium constant, while $K^{\ominus}=1/P_{H_2}$ in hydriding process.

$$\ln K^{\ominus} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{Eq.(3)}$$

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