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The high capacity and controllable hydrolysis rate of Mg₃La hydride

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ABSTRACT

This paper reports the synthesis of Mg_3La alloys with different hydrogenation degree through controlling the hydrogen amount introduced and reveals the hydrogenation mechanism. The hydrolysis rate and hydrogen yield of Mg_3La hydride could be controllable through adjusting the ratio of LaH_3 to Mg or MgH_2 . The fully hydrogenated Mg_3La alloy can generate 873.24 ml g⁻¹ in 66 min (7.80 wt.%). The results show that the hydrolysis performance of MgH_2 in Mg_3La hydrides could be significantly accelerated by LaH_3 while that of Mg was affected limitedly by LaH_3 .

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1. Introduction

As the development of economy and expansion of population, the global energy supplies issues face the social, economic and environment problems [1]. Hydrogen is considered as a promising energy carrier because it is high energy density (142 MJ kg⁻¹), lightweight (0.0899 g l⁻¹) and environmentally benign product of oxidation (water) [2,3]. The feasible method for hydrogen production is especially important for the realization of hydrogen economy.

Hydrolysis is an efficient and convenient hydrogen generation method for low operation temperature, pure hydrogen, high hydrogen yield and simple reaction equipment [4]. Hydrolysis materials can be divided into metal [5–7], metal hydride [8–10], chemical hydride [11–13] and so on. Hydrolysis of magnesium hydride with hydrogen yield 15.2 wt.% is cheap, available raw material and environment friendly process which only produce $Mg(OH)_2$ besides pure hydrogen gas [14,15]. Therefore, Hydrolysis of magnesium hydride as hydrogen resource is a promising method for on-board vehicular or portable application. However, the hydrolysis of MgH₂ is easy to be rapidly interrupted because the formation of a low water solubility magnesium hydroxide layer to inactive material [16]. Hence, ball-milled magnesium hydride composites have to be performed in aqueous/alcoholic solution [17-19], acid solution [20] or using ultrasonic irradiation [9] to improve the hydrolysis properties, but they would pollute the environment, corrode the equipment or had to design extra ultrasonic equipment which needs extra energy supplied. The author had found that LaH₃ could significantly improve the hydrolysis of MgH_2 [21] and the $LaMg_{12}$ hydrides with controllable hydrolysis rate had also been explored by adjusting the different hydrogenation degree of LaMg₁₂ alloys [10]. But the whole hydrolysis rate of LaMg₁₂ hydrides is relatively slow. Due to LaH₃ play the key role in the hydrolysis of MgH₂, the hydrolysis performance of MgH₂ can be further improved by increasing the amount of LaH₃ on the base of LaMg₁₂ hydrides to meeting the hydrogen generation rate for commercial utilization. Hence, in this work, the controllable and effective hydrolysis materials, Mg₃La alloys with different hydrogenation degree, were prepared through controlling the relative ratio of the in situ formed LaH₃ to Mg/MgH₂ phases.

2. Experiment section

2.1. Sample preparation

The high purity Mg (99.9%) and La (99.9%) were using to prepare Mg₃La alloy by induction melting at pure Ar atmosphere. The obtained alloy was ball-milled on a QM-SP1 planetary ball mill rotating at 350 rpm for 1 h with the ball-to-powder mass ratio of 20:1. All samples were performed in an Ar filled glove box in order to prevent them from oxidation or hydrolysis.

The samples of different hydrogenation degree were carried out on a gas reaction controller of AMC (Advanced Materials Corporation). Each sample was hydrogenated about 2.5 h under the pattern of Auto soak (small) with the different initial hydrogen pressures. The hydrogenated alloys reacted with pure water in a 250 ml Pyrex glass reactor following the previous method [21].



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2.2. Samples characterization

The phase structures of samples were obtained on Philips X'Pert diffractometer using graphite monochromatized Cu K α radiation as the light source. A scanning rate of 0.02°s⁻¹ was applied to record the patterns in the 2 θ range of 15–90°. The powder samples were covered with paraffin oil to prevent oxidation during measurements. The XRD profiles were analyzed by the Rietveld method with the program of X'Pert HighScore Plus to determine the strain and grain size [10].

3. Results and discussion

3.1. Preparation of Mg_3LaH_3 , Mg_3LaH_6 and Mg_3LaH_9 by controlling the hydrogenation degree

Fig. 1 shows the XRD patterns of the ball-milled and three kinds of materials with the rations being 3, 6 and 9 of H to Mg₃La named Mg₃LaH₃, Mg₃LaH₆ and Mg₃LaH₉. Fig. 1a shows the X-ray diffraction pattern of Mg₃La alloy after ball milling. All diffraction peaks can be attributed to Mg₃La phase (ICPDS Card, No. 65-0919), which can be indexed as D03 structure. This result showed that no other phase existed in the alloy. Fig. 1b shows the X-ray diffraction pattern of Mg₃LaH₃, in which the peaks can be indexed as LaH₃ phase with a face-centered cubic structure and Mg phase with closepacked hexagonal structure. No peak corresponding to the MgH₂ phase in the XRD patterns confirmed that La reacted with hydrogen prior to Mg and form LaH₃ due to that La had more affinity with hydrogen than that of Mg. And no peak in accordance with Mg₃La phase indicated that all the Mg₃La phase had transited to LaH₃ and Mg phases during the hydrogenation process. The hydrogenation reaction can be described as Eq. (1):

$$Mg_{3}La + 3/2H_{2} \rightarrow LaH_{3} + 3Mg \tag{1}$$

 Mg_3LaH_6 and Mg_3LaH_9 were also prepared by gradually increasing the amount of introduced hydrogen. Fig. 1c and d show the Xray diffraction patterns of Mg_3LaH_6 and Mg_3LaH_9 , respectively. The peaks of the Mg_3LaH_6 alloy in XRD patterns were attributed as LaH_3 , MgH_2 and Mg phase. Apparently, part of Mg started to absorb hydrogen and form MgH_2 while LaH_3 still kept the same fashion. The existence of Mg peaks as shown in Fig. 1b and c indicated that both Mg_3LaH_3 and Mg_3LaH_6 alloys were only partially hydrogenated. The diffraction peaks of Mg_3LaH_9 can be indexed as LaH_3 and MgH_2 phase. No existence peaks of Mg phase as shown in Fig. 1d indicated that Mg_3La alloy had fully reacted with hydrogen and formed LaH_3 and MgH_2 phases. The corresponding reactions are shown in Eqs. (2) and (3), respectively.



Fig. 1. The XRD patterns of ball milled Mg₃La alloys (a), partially hydrogenated Mg₃LaH₃ (b), Mg₃LaH₆ (c) and fully hydrogenated Mg₃LaH₉ (d) at 573 K.

$$Mg_{3}La + 6/2H_{2} \rightarrow LaH_{3} + 3/2MgH_{2} + 3/2Mg \tag{2}$$

$$Mg_3La + 9/2H_2 \rightarrow LaH_3 + 3MgH_2 \tag{3}$$

Judging from the corresponding reactions as shown in Eqs. (1)-(3), the hydrogenation steps of Mg₃La were that La first reacted with hydrogen to form LaH₃ and then Mg reacted with H to form MgH₂ after all La had reacted with H.

3.2. Hydrolysis properties of Mg₃LaH₃, Mg₃LaH₆ and Mg₃LaH₉

Fig. 2 shows the hydrogen evolution curves of Mg₃LaH₃, Mg₃₋ LaH₆ and Mg₃LaH₉ alloys at 298 K, respectively. As shown in Fig. 2a, Mg_3LaH_3 produced 443.39 ml g⁻¹ hydrogen in 3 min and up to 452.83 ml g^{-1} in 59 min in the hydrolysis process. For the hydrolysis of Mg₃LaH₆ alloy, as presented in Fig. 2b, the conversion yield was 455.45 ml g^{-1} in 2 min and released to 618.81 ml g^{-1} in 73 min. But the hydrolysis rate of Mg₃LaH₉ alloy had a great change. Mg_3LaH_9 generated 586.85 ml g⁻¹ of hydrogen in 3 min and quickly up to 685.45 ml g⁻¹ in 22 min then continued to generate 873.24 ml g⁻¹ in 66 min (Fig 2c). The final hydrogen yield of hydrolysis reaction of Mg₃LaH₃, Mg₃LaH₆ and Mg₃LaH₉ were 4.04 wt.%, 5.52 wt.% and 7.80 wt.%, respectively. Conversion into equivalent mole amount, 4.34 mol H₂, 6.02 mol H₂ and 8.61 mol H₂ can be generated by hydrolysis of per mole of Mg₃LaH₃, Mg₃ LaH₆ and Mg₃LaH₉, respectively. The hydrogen produced was greater than that in H-Mg₃La itself, indicating that this extra part of hydrogen generated from that in water. The results illustrated that the hydrolysis of metal hydride was an effective method for hydrogen generation compared with that of metals and/or alloys.

Fig. 3 shows the grain sizes and strains of LaH₃, MgH₂ and Mg in Mg₃LaH_x. The sizes of LaH₃, MgH₂, Mg phases in the different hydrides of Mg₃LaH₃, Mg₃LaH₆ and Mg₃LaH₉ were in the same order of 50 ± 10 nm, respectively. Also, the strains of LaH₃, MgH₂, Mg phases in the different hydrides were similar, which were in the same order of 0.2 ± 0.1 %. Hence, it can be concluded that the improvements of hydrolysis performances had rarely relation with the sizes and strains of LaH₃, MgH₂, Mg phases.

In order to reveal the hydrolysis mechanism of Mg_3LaH_x , the hydrolysis products of Mg_3La hydrides can be analyzed by XRD, as shown in Fig. 4. Fig. 4a shows the XRD diffraction pattern of hydrolysis product of Mg_3LaH_3 . The new appeared peaks can be detected as $Mg(OH)_2$ and $La(OH)_3$ while the peaks of the original LaH_3



Fig. 2. The hydrogen evolution curves of the hydrolysis for (a) Mg_3LaH_3 , (b) Mg_3LaH_6 and (c) Mg_3LaH_9 at 298 K. Hydrolyses of Mg_3LaH_3 , Mg_3LaH_6 and Mg_3LaH_9 generated 452.83 ml g⁻¹, 618.81 ml g⁻¹ and 873.24 ml g⁻¹ in the end, with total hydrogen yields of 4.04 wt.%, 5.52 wt.% and 7.80 wt.%, respectively.



Fig. 3. The sizes and strains of LaH₃, MgH₂ and Mg in Mg₃LaH₃ (X = 3), Mg₃LaH₆ (X = 6) and Mg₃LaH₉ (X = 9), respectively. The sizes/strains of LaH₃ in Mg₃LaH₃, Mg₃LaH₆, and Mg₃LaH₉ are 39 nm/0.23%, 60 nm/0.23% and 43 nm/0.32%, respectively. The sizes/strains of MgH₂ in Mg₃LaH₆ and Mg₃LaH₉ are 52 nm/0.14% and 46 nm/0.17%, respectively. And the sizes/strains of Mg in Mg₃LaH₃ and Mg₃LaH₆ are 51 nm/0.18% and 48 nm/0.21%, respectively.



Fig. 4. The XRD patterns of the hydrolysis production of (a) $Mg_3LaH_3,$ (b) Mg_3LaH_6 and (c) $Mg_3LaH_9.$

and Mg phases still existed, which indicated that the Mg₃LaH₃ only partially hydrolyzed. As we know, pure LaH₃ can react with water completely. However, only partial LaH₃ could react with water in Mg₃LaH₃ indicated that the coexisted Mg could partially prevent the LaH₃ from being hydrolyzed in water. It can be also indicated that hydrolysis performance of Mg was affected limitedly by LaH₃. For the hydrolysis of Mg₃LaH₆, the newly appeared peaks in the XRD pattern could also be indexed as Mg(OH)₂ and La(OH)₃ phases. All the LaH₃, MgH₂ and Mg phases in Mg₃LaH₆ had disappeared. Likewise, both LaH₃ and MgH₂ phases disappeared and the newly peaks can be attributed as Mg(OH)₂ and La(OH)₃ phases after the hydrolysis of Mg₃LaH₉ as shown in Fig. 4c. In the case of hydrolysis of Mg₃LaH₆ and Mg₃LaH₉, it can be illuminated that LaH₃ can significantly accelerate the hydrolysis of MgH₂.

Based on that the LaH_3 content was the same but the MgH_2 and $Mg\,$ were various in different hydrides, the hydrolysis rate of

 Mg_3LaH_9 was quickest among Mg_3LaH_3 , Mg_3LaH_6 and Mg_3LaH_9 . As the hydrogenation degree rose, the content of MgH_2 increased and Mg content decreased. The hydrolysis performance of MgH_2 could be significantly accelerated by LaH_3 but that of Mg was affected by LaH_3 limitedly. For the fully hydrogenated Mg_3LaH_9 sample, the coexisted LaH_3 and MgH_2 promoted each other which resulted in complete hydrolysis. Hence, the hydrolysis rate and yield of Mg_3LaH_x hydride could be controlled through adjusting the ratio of LaH_3 to Mg or MgH_2 . Compared to the hydrogenated $LaMg_{12}$ [10], the fully hydrogenated Mg_3La had the higher hydrolysis rate due to the higher ratio of LaH_3 to MgH_2 . So Choosing the hydride with suitable ratio of La:Mg is also important to get the optional hydrolysis rate for commercial application.

4. Conclusion

Control the amount of hydrogen involved the reactions can obtain different hydrogenated degree Mg₃La alloys. La first adsorbed hydrogen and transformed into LaH₃, after that Mg element reacted with hydrogen and transformed into MgH₂. The hydrolysis performance of MgH₂ could be significantly accelerated by LaH₃ but Mg was affected by LaH₃ limitedly. The fully hydrogenated Mg₃La alloy can generate 873.24 ml g⁻¹ H₂ in 66 min (7.80 wt.%). The hydrolysis rate and yield of Mg₃La hydride could be controllable through adjusting the ratio of LaH₃ to Mg or MgH₂.

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