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EFFECT OF ANNEALING TIME ON THE STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF $LA_{0.70}MG_{0.30}NI_{2.45}CO_{0.75}AL_{0.30}$ HYDROGEN STORA GE ALLOY

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The as-cast alloy with the composition of $La_{0.70}Ni_{2.45}Co_{0.75}Al_{0.30}$was prepared by melting. La-Mg-Ni-based $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ hydrogen storage alloy has been synthesized by milling blending of the as-cast alloy andelemental Mg, followed by an annealing for x (x= 2, 4, 6 and 8 h) at 600℃. The effect of annealing time on the structure and electrochemical properties of $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ hydrogen storage alloy was investigated. The results showed that the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys contain the $LaNi_5$ and $(La,Mg)_2Ni_7$. The maximum discharge capacity of the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloy increases first and then decreases with increasing annealing time. The maximum discharge capacity of alloy reaches the optimumwhen *x* is 4 h. The cyclic stability of the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloy for a longer annealing time is better than that of the alloy for a shorter annealing time.
Keywords: La-Mg-Ni-based hydrogen storage alloy; Annealing time; Microstructure; Electrochemical property

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Сплав с составом $La_{0.70}Ni_{2.45}Co_{0.75}Al_{0.30}$готовили путем плавления. La-Mg-NiиLa$_{0.70}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Al$_{0.30}$сплав для хранения водорода синтезирован путем размола при смешении в литом сплаве с элементарнымMg, с последующим отжигом при разных временах отжига x (x = 2, 4, 6 и 8 ч) при температуре 600 °C. Было исследовановлияние времени отжига на структуру и электрохимические свойства сплава для хранения водорода. Результаты показали, что сплавы содержат $LaNi_5$ и $(La, Mg)_2Ni_7$. Максимальная разрядная емкость из сплава возрастает, а затем уменьшается с увеличением времени отжига. Максимальная разрядная емкость сплава достигает оптимума, когда x=4ч. Циклическая стабильность полученного сплава в течение времени лучше, чем у сплава с более коротким временем отжига.
Ключевые слова: La-Mg-Ni сплав для хранения водорода,время отжига, микроструктура,электрохимические свойства.

1. Introduction

In recent years, the superlattice structure La-Mg-Ni-based hydrogen storage alloyshows considerable potential for hydrogen storage due to their relatively high hydrogen storage capacity, low cost and good activation performance [1-3]. However, La-Mg-Ni-based alloy has not been commercialized because of its difficult synthesis and poor electrochemical cyclic stability [4,5]. The La-Mg-Ni-based $La_{0.70}Mg_{0.30}Ni_{2.45}Co_{0.75}Al_{0.30}$ hydrogen storage alloywas synthesized by a new method in this work. Firstly, other alloy elements without metal Mg in the La-Mg-Ni-based alloy were melted by melting method and the as-cast alloy was obtained. Secondly, the La-Mg-Ni-based alloy powders were prepared by high-energy milling the mixture of the as-cast alloy and a certain amount of Mg. Finally, the above milled La-Mg-Ni-based alloy powders were annealed at 600℃for different annealing time. The effect of annealing time on the structure and electrochemical properties of the La-Mg-Ni-based alloy is studied in detail.

2. Experimental

The $La_{0.70}Ni_{2.45}Co_{0.75}Al_{0.30}$ as-cast alloy was prepared bymelting. The powders of that were mixed with an appropriate amount of Mg powders in accordance to $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$. The obtained powder mixtures with the composition of $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ were subsequently milled in milling machine for 2 h. After milling, the milled powders were annealed at 600℃for x (x= 2, 4, 6 and 8 h)under the argon atmosphere. The phase composition of the sample was performed by XRD. The morphology of the sample and the corresponding Mg element distributing in the sample was characterized by SEM. The measurement of the electrochemical property of sample was the same with our previous study [6].

3. Results and discussion

The XRD patterns of samples are shown in Fig. 1. It can be found that only $LaNi_5$ phase is observed in the as-cast $La_{0.70}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloy. However, the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys consist of the $LaNi_5$ main phase and a small amount of $(La,Mg)_2Ni_7$ new phase. Fig. 2 presents the SEM micrographs and the corresponding Mg element distribution of the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$alloy annealed for different annealing time. The bright spots in the micrographs are just the Mg elements distribution in the alloys. It can be observed from Fig. 2 that the morphologies of the alloys exhibit an alveolate surface morphology. Moreover, the bright spots in the micrograph of the alloy annealed for 4 h obviously increase. It implies that the content of Mg is most abundant in the alloy annealed for 4 h.

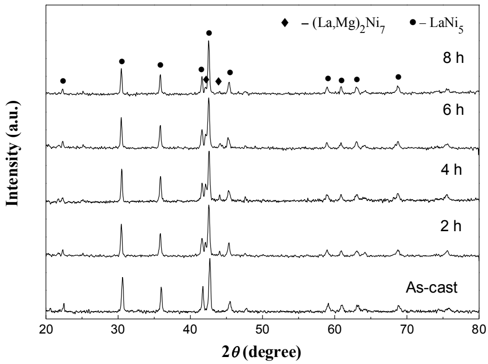

Fig. 1 XRD patterns of the as-cast $La_{0.70}Ni_{2.45}Co_{0.75}Al_{0.30}$ and $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys

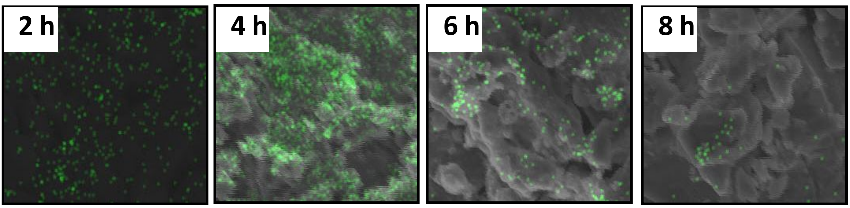

Fig. 2 SEM micrographs and the corresponding Mg elementdistributing of the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys annealed for different time

Fig. 3 shows variations of discharge capacity with cycle number for the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys. The main electrochemical properties of the alloys are summarized in Table 1. It can be seen that the alloys showed good activation performance.The maximum discharge capacity of the alloy first increases then decreases with increasing annealing time. The maximum discharge capacity of the alloy annealed for 4 h attained a maximum value. The content of Mg in the alloy is directly related to annealing time. The above result indicates that appropriate content of Mg in the alloy can effectively improve the discharge capacity of the alloy. Furthermore, the capacity retaining rate of the alloy annealed for longer time (6 h and 8 h) is obviously higher than that of the alloys annealed for shorter time (2 h and 4 h). The improvement of cycling stability of the alloy might be mainly attributed to a smaller quantity of Mg in the alloy caused by annealing for a long time, because the more content of magnesium in the alloy exists, the worse cyclic stability of the La-Mg-Ni-based alloy follows.

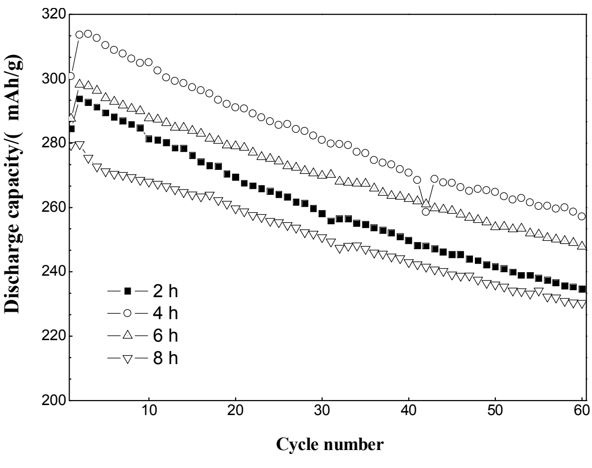

Fig. 3 Variations of discharge capacity with cycle number for the $La_{0.70}Mg_{0.3}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys

Table 1

The main electrochemical properties of $La_{0.70}Mg_{0.30}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys

Samples	N_a	C_{max} / (mAh/g)	C_{60} / (mAh/g)	S_{60} / (%)
x= 2 h	2	293.7	234.6	79.8
x=4 h	3	313.5	247.8	79.0
x= 6 h	2	298.2	247.8	83.1
x= 8 h	2	279.6	230.3	82.3

4. Conclusions

A novel preparation method for the La-Mg-Ni-based alloy was proposed in this paper. The structure and electrochemical properties of the prepared alloys have been examined. The conclusions can be summarized as follows: the $La_{0.70}Mg_{0.30}Ni_{2.45}Co_{0.75}Al_{0.30}$ alloys all were composed of $LaNi_5$ phase and $(La,Mg)_2Ni_7$ phase. The maximum discharge capacity of the alloy first increases then decreases with increasing annealing time. Thecapacity retaining rate of the alloy annealed for longer time is obviously higher than that of the alloys annealed for shorter time.

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