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Electrochemical Hydrogen Storage Properties of Sintered $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ Alloy

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The $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy was synthesized by arc-melting and powder sintering techniques and the microstructure and electrochemical performance of the alloy were investigated. The results showed that the alloy mainly consist of the (La, Mg) Ni_3 and the $LaNi_5$ phases and the powder sintering time made a different effect on the electrochemical hydrogen storage properties, when the alloy sintered at 1173 K for 4 h, it exhibited a maximum discharge capacity of 334 mAh/g and the sintered alloy for 10 h showed a best cyclic stability, the cycling capacity retention rate was 69.1 % after 100 cycles.

Key Words: AB_3-type alloy, Sinter, Hydrogen storage, Electrochemical properties.

INTRODUCTION

Nowadays, developing new type hydrogen storage alloy which has large hydrogen storage capacity, excellent discharge dynamics performance, low cost and pollution-free to substitute for the traditional $LaNi_5$ base hydrogen storage alloy has become the focus of study. RM_3 (R = rare earth elements, Ca, Mg and 3, 4 group element, M = Ni, Fe, Cu, Co, Zn, *etc*.) hydrogen storage alloy which has $PuNi_3$ type structure has aroused widespread concern of scholars globally owing to its special structure, large hydrogen storage capacity and excellent alloy electrode dynamic performance advantages[1-3]. Especially AB_3-type hydrogen storage alloy containing Mg, its maximum discharge capacity can reach 400 mAh/g above which is 1.3 times as large as AB_3-type alloy, thus, it has been received wide concern.

Kadir *et al.*[4] synthesized many new type ternary magnesium base alloys through mixed reaction of $MgNi_2$ and intermetallic compound RNi_5 (R = La, Ce, Pr, Nd, Sm and Gd) or direct combination according to the atomic ratio R:Mg:Ni = 1:2:9. Kohno *et al.*[5] studied new type La-Mg-Ni alloy: La_2MgNi_9, $La_5Mg_2Ni_{23}$ and La_3MgNi_{14} systems with hydrogen storage properties, $La_{0.67}Mg_{0.33}Ni_{2.5}Co_{0.5}$, $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$, $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$ alloys were produced by the method of induction smelting in argon gas, then the sucking/putting hydrogen characteristics of these alloys were studied. The results showed $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$ exhibited more discharge capacity (410 mAh/g), which was 1.3 times as large as $LaNi_5$ system alloy (320 mAh/g), the discharge capacity of other alloys are also larger than $LaNi_5$ system alloy. Since 2000, Pan *et al.*[6] reserched the influence of different heat treatment process on the electrochemical properties of $La_{0.67}Mg_{0.33}Ni_{2.5}Co_{0.5}$ alloy. After annealing, alloy electrode showed excellent activated performance (two times), its maximum discharge capacity could reach 397.5 mAh/g. The high rate discharge capacity was better than that of $LaNi_5$-based hydrogen storage alloy, but the alloy electrode looping stability was poor.

Zhao *et al.*[7] studied the electrochemical properties of $La_{0.7}Mg_{0.3}Co_{0.45}Ni_{2.55}$-$xFe_x$(x = 0-0.4) hydrogen storage alloys prepared by rapid quenching method, the maximum discharge capacity of alloy decreased, but the cycle life was significantly improved. An *et al.*[8] reserched the properties of $La_{0.7}Mg_{0.3}Ni_{2.5+x}Co_{0.5}$ alloys, the maximum discharge capacity of this series of hydrogen storage alloys increased with the increase of x value, the maximum value could reach 377.5 mAh/g and they had good activation performance. Zhang *et al.*[9] studied the electrochemical hydrogen storage properties of $La_{0.75}Mg_{0.25}Ni_{3.5}M_x$ (M = Ni, Co; x = 0-0.6), the maximum discharge capacity could reach 401.8 mAh/g.

The cycle stability of the hydrogen storage alloy is an important performance index of Ni-MH battery. Battery failure shows that capacity reduces, discharge voltage decreases,

battery storage energy declines in the high rate discharge process[10]. The alloy may be pulverized in the charging and discharging process, the surface of the alloy may be corroded and oxidized, thus, the contents of Mg and La in the alloy will be sharply declined, which makes the hydrogen absorbing ability of alloy decline and its cycle life is poor. Therefore, to improve the cycle life of AB_3-type alloy and maintain the discharge capacity of the alloy become the focus of research and development of this series alloy. In this paper, $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ alloy was synthesized by mixed powder sintering and the prepared technology and structual characteristic were researched in order to obtain the best electrochemical hydrogen storage properties of this alloy.

EXPERIMENTAL

La, Mg, Ni, Co, Al and Mn were used as raw materials, their purities were all higher than 99 %. Firstly, Mg_3La and $MgNi_2$ two kinds of intermetallic compounds were produced in the induction furnace, then $LaNi_{4.2}Co_{0.6}Mn_{0.3}Al_{0.15}$ alloy was synthesized in the electric arc furnace. These three above-mentioned kinds of intermediate alloys were ground into powder, then mixed uniformly according to the proportion of ingredients of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ and cold press molded. High-temperature sintering was conducted under argon atmosphere, the sintering temperature was 1173 K.

General procedure: Sample was pulverized mechanically and the powders were sieved to 275 mesh, then the powder was served for electrochemical properties test. 0.150 g hydrogen storage alloy powder and 0.750 g carbonyl nickel powder were weighed accurately and well-mixed, then compressed to form cylinders with 1 mm height and 9 mm diameter by a uniaxial single-acting press at 15 MPa.

Detection method: Phase composition of alloy was analyzed by XRD apparatus (Rigaku D/max-2500, 50 kV, 200 mA, Japan) with CuK_{α}_ radiation. Electrochemical properties of alloy electrode were measured by dual electrode system, the auxiliary electrode was sintered type nickel anode [$Ni(OH)_2$/NiOOH]. A deaerated 6 mol/L KOH solution was used as electrolyte and all measurements were performed in a temperature-controlled bath in the range of (303 ± 0.5) K. Alloy electrode of the maximum discharge capacity, activation performance, high discharge rate (HRD) and cycle stability were measured on a battery tester (DC-5, Shanghai affirmative company).

RESULTS AND DISCUSSION

Structure of alloy: Fig. 1 showed the XRD patterns of the alloy in different sintering time. It could be seen that each phase of the alloy had obvious change with the sintering time increase. When the sintering time reached to 4 h, there were a lot of $LaNi_5$ phase in the alloy and had a small amount of Mg_3La and $MgNi_2$ phase. The content of (La, Mg)Ni_3 phase in alloy increased gradually with the sintering time continued to increase. When the sintering time reached to 10 h, the alloy mainly consist of the $LaNi_5$ and the (La, Mg)Ni_3 phases.

Electrochemical hydrogen storage properties: Alloy electrode was charged 8 h with 60 mA/g constant current, standing for 10 min, then discharged with 60 mA/g constant

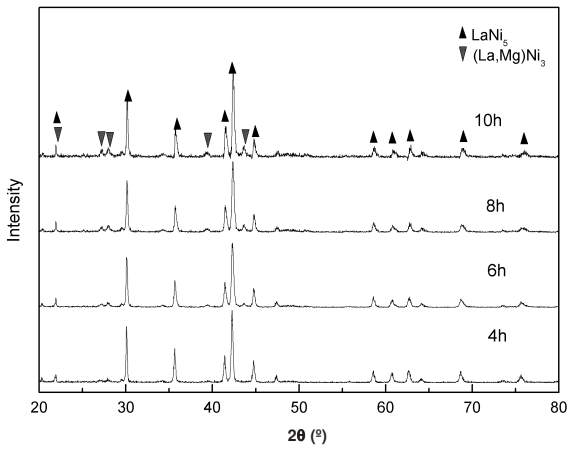

Fig. 1. XRD patterns of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ alloy (sintering time: 4, 6, 8 and 10 h)

current, until the voltage reached to 0.8 V. The alloy electrode should be stood for 10 min after one charge-discharge cycle and then proceeded to next cycle. Under this charge and discharge system, when the electrode obtained the maximum discharge capacity, the number of cycles required was the number of activation of the alloy electrode. Experiments revealed the alloy reached the maximum discharge capacity in 5 cycle period, its activation performance was well. The maximum discharge capacity of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ alloy was shown in Fig. 2. From which we could see, the maximum discharge capacity increased firstly and then decreased gradually with the increase of sintering time. It increased from 322 mAh/g (not sintered) to 334 mAh/g (1173 K, sintering for 4 h), then decreased to 297 mAh/g (1173 K, sintering for 10 h) gradually.

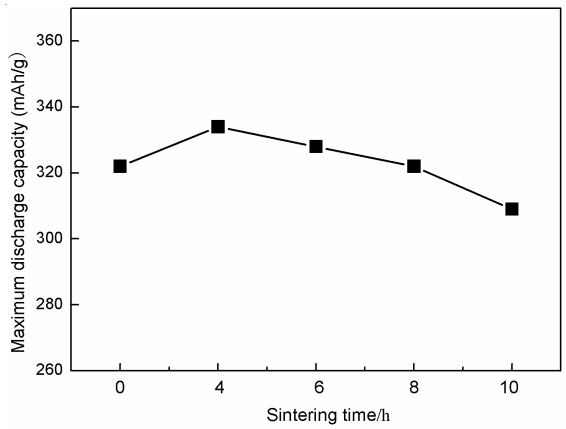

Fig. 2. Maximum discharge capacity of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ alloy (sintering time: 0, 4, 6, 8 and 10 h)

The change of the alloy electrode electrochemical properties depends on the proportions of the various phases in the alloy. $LaNi_3$ phase contributes to enhancing the maximum discharge capacity of the alloy and $LaNi_5$ phase helps to improve catalytic activity of the alloy. But in the process of experiment, it could be found that the maximum discharge capacity of alloy electrode decreased with the increase of $LaNi_3$ phase. Perhaps, the volatilization of Mg element and the decrease of the specific surface area hydrogen storage alloy

particles in the sintering process were the main reasons of the decrease of the maximum discharge capacity of alloy.

After fully being activated, alloy electrode was charged 8 h with 60 mA/g constant current, standing for 10 min, then it was discharged with 300, 600, 900 and 1200 mA/g constant current, respectively, until the voltage reached 0.8 V, standing for 10 min. After that, it should be charged and discharged one time in 60 mA/g constant current. The ratio HRD_h (h = 300, 600, 900, 1200) of the discharge capacity under different current densities to the total discharge capacity (the sum of the discharge capacity under different current densities and the discharge capacity under 60 mA/g current density) was used to indicate the high rate discharge performance of the alloy electrode.

Fig. 3 showd the high rate discharge performance of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy synthesized in different sintering time. As shown in the figure, the high rate discharge performance of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy first increased and then decreased with the sintering time increase. The HRD_{900} of the samples sintered for 8 h reached to 95.4 %, then decreased to 94.9 % when sintered for 10 h. As mentioned previously, the change of the alloy electrode electrochemical properties caused by the different sintering time depended on the proportions of the various phases in the alloy. With the increase of sintering time, the (La, Mg)Ni_3 phase of the alloy increased to some extent and the $LaNi_5$ phase decreased, which resulted in the overall catalytic activity of the alloy decreasing. The too long sintering time was the main reason leading to the decrease of the high rate discharge performance of the alloy electrode.

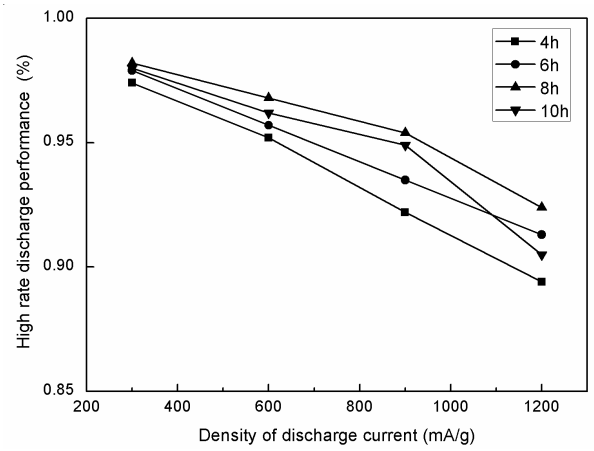

Fig. 3. HRD of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ alloy (sintering time: 4, 6, 8 and 10 h)

The activation of the alloy electrode was repeated in the following process: the alloy electrode was charged at 200 mA/g for 4 h, followed by resting for 10 min. Then it was discharged at 200 mA/g to a cut-off potential of 0.8 V, followed by resting for 10 min. The S_{100} (capacity, %) characterizes the cycle stability of alloy electrodes. Fig. 4 showed charge and discharge cycle characteristics of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy produced of different sintering time. As shown in the figure, the cycle stability of alloy electrodes increased with the increase of sintering time. which increased from 63.0

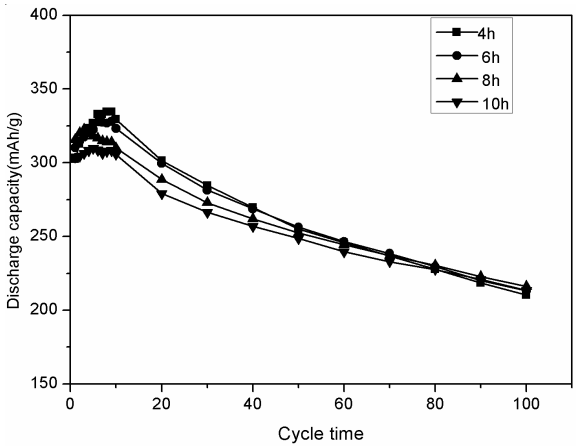

Fig. 4. Cycle life curves of $La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy electrodes (sintering time: 4, 6, 8 and 10 h)

to 69.1 %. It indicated that the increase of sintering time could effectively improve the cycle stability of the alloy.

Conclusion

$La_{0.7}Mg_{0.3}Ni_{2.5}Co_{0.4}Mn_{0.2}Al_{0.1}$ hydrogen storage alloy synthesized by mixed powder sintering was multiphase structure. It mainly consisted of $LaNi_5$ and (La, Mg)Ni_3 phases. The content of (La, Mg)Ni_3 phase increased and the content of $LaNi_5$ phase decreased with the increase of sintering time. Different sintering time had a great influence on the electrochemical properties of the alloy. With the increase of sintering time, the maximum discharge capacity increased firstly and then decreased gradually and it reached to maximum 334 mAh/g when alloy was sintered for 4 h. The alloy could reach the maximum discharge capacity in 5 cycles and its activation performance was well. The high rate discharge performance of the present alloy firstly increased and then decreased and it reached to maximum when alloy was sintered for 8 h. The cycle stability of alloy could be improved with the extending sintering time.

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