MICROSTRUCTURE AND ELECTROCHEMICAL PERFORMANCE OF LaMgAlMnCoSnNi ALLOYS ALLOYS FOR NICKEL – METAL HYDRIDE BATTERIES

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ABSTRACT

The effects of substitution of Sn for Co on the microstructure and electrochemical discharge capacity of $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ *(x = 0.0, 0.2 and 0.5) alloys were investigated. Microstructure and phase composition of samples were investigated employing scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results showed that all of alloys are mainly composed of* $LaNi_5$ *and* $MgNi_2$ *phases, but when increasing the content of Sn in alloys the LaNiSn phase appears. The electrochemical discharge capacity were investigated by charging and discharging the negative electrode alloys. Tests indicated that the maximum discharge capacity decrease from 337.1 mAh/g (x = 0.0) to 249.8 mAh/g (x = 0.5).*

Keywords: Hydrogen storage alloys, Microstructure, Ni-MH batteries.

INTRODUCTION

Over the past years, $LaNi_5$-based hydrogen storage alloys for use in electrodes of rechargeable batteries have systematically incorporated specific alloying elements to improve the kinetics of hydrogen absorption and desorption, increase cycle life, improve corrosion resistance, etc. Cobalt, aluminum, manganese and magnesium are invariably present in the alloy composition [1].

In the literature there are several examples of Co-free and Low-Co AB_5 type alloys. Ferreira and co-workers investigated the influence of substitution of Co by Nb on $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}X_{0.5}Ni_{3.8}$ (x = Co, Nb) alloys. Results showed that $NbNi_3$ phase appear on the microstructure and the discharge capacity decrease from 324 mAh/g (Co) to 221 mAh/g (Nb) [2].

Few investigations had published based on substitution of Sn for Ni [3 - 5]. For example, Kumar et al. [5] reported a favorable charge-discharge cycling stability and good discharge capacity on the $LaNi_{4.25}Co_{0.5}Sn_{0.25}$ alloy. In this paper, the microstructure, phase identification, electrochemical capacity and cycling stability of AB_5 type $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ hydrogen storage alloys have been investigated systematically.

EXPERIMENTAL

The nominal composition of the studied alloys were designed as $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5). The purity of all elements were at least 99.9%. The alloys were prepared by induction melting in a water-cooled copper crucible under the protection of argon atmosphere. The ingots were re-melted twice for homogeneity.

In order to investigate the morphology and composition of the alloy, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometer (EDS) was used.

All tests electrodes were prepared by mixing alloy powder and nickel powder (<3μm) with weight ratio of 1:4. The mixture was cold pressed under a pressure of 15 MPa (about 1cm^2 in area and 0.1 mm in thickness). The discharge capacity of each electrode was measured in a flooded cell configuration using $Ni(OH)_2/NiOOH$ as a counter electrode and 6 M KOH solution as the electrolyte. The system was charged at 100 mA/g for 5 h followed by a 10 min rest and then discharged at 50 mA/g to the cut-off potential of 0.8 V.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM micrographs of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5) hydrogen storage alloys. Combined the results SEM micrographs and EDS (Table 1) analysis show the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5) alloys are composed of La and Ni rich phase ($LaNi_5$-phase, light grey regions), Mg and Ni rich phase ($MgNi_2$-phase, dark regions) and La, Sn and Ni rich phase (LaNiSn-phase, white regions) with small quantities of Mg content. As shown in Fig. 1(a) the composition of La, Mg and Ni ($(La,Mg)Ni_3$-phase, dark grey regions), which is similar to the results reported by Zhang et al. on the $La_{1.3}CaMg_{0.7}Ni_{9-x}(Al_{0.5}W_{0.5})_x$ alloys [6]. When increasing the content of Sn, the content of LaNiSn phase increased gradually and more fine grains found, which is similar for $LaNi_{4.0}Al_{0.2}Fe_{0.4}Cu_{0.4-x}Sn_x$ alloys studied by Jiangyuan et al [7]. The further research would be studying the influence annealing treatment in these alloys.

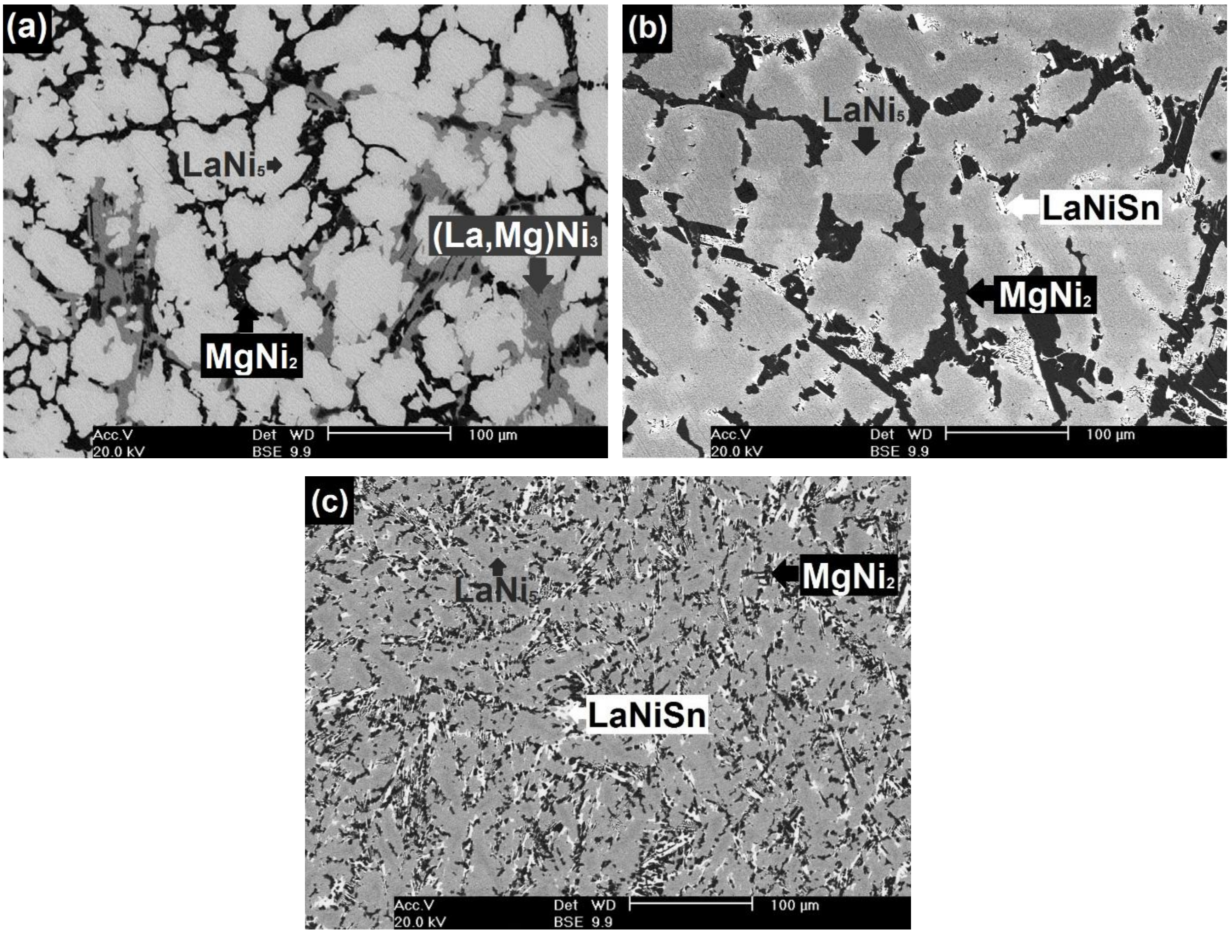

Figure 1 - SEM micrographs of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ alloys: (a) X = 0.0, (b) X = 0.2 and (c) X = 0.5.

Table 1 - EDS results for different phases identified in SEM micrographs.

Sample	Phase	Elements (at%)						
		La	Mg	Al	Mn	Co	Sn	Ni
X = 0.0	$LaNi_5$	15.4	<1	4.5	2.5	7.9	-	69.5
	$MgNi_2$	<1	19.8	3.3	12.6	8.5	-	54.9
	$(La,Mg)Ni_3$	8.4	10.3	2.8	6.9	8.0	-	63.6
X = 0.2	$LaNi_5$	15.3	<1	4.9	3.2	4.9	3.2	67.9
	$MgNi_2$	<1	21.2	3.3	10.7	6.5	<1	57.3
	LaNiSn	19.4	3.2	2.4	4.1	2.6	19.7	48.6
X = 0.5	$LaNi_5$	15.7	<1	4.4	3.5	-	6.9	68.9
	$MgNi_2$	<1	21.7	3.5	11.8	-	<1	61.5
	LaNiSn	19.8	4.1	2.3	3.2	-	20.4	50.2

Fig. 2 shows the cycle life curves of the alloy electrodes. The maximum discharge capacities (C_{max}) of the electrode alloys are summarized in Table 2. It can see clearly that electrochemical capacity decreased markedly from 337.1 mAh/g (x = 0.0) to 249.8 mAh/g (x = 0.5) with the increase in Sn content. These results are similar to $MlNi_{(4.45-x)}Mn_{0.4}Al_{0.15}Sn_x$ reported by Jianxin et al. [8]. The discharge capacity of the $MlNi_{(4.45-x)}Mn_{0.4}Al_{0.15}Sn_x$ electrode alloys decreased from 343.2 mAh/g (x = 0.0) to 235.4 mAh/g (x = 0.5) with increase of Sn content.

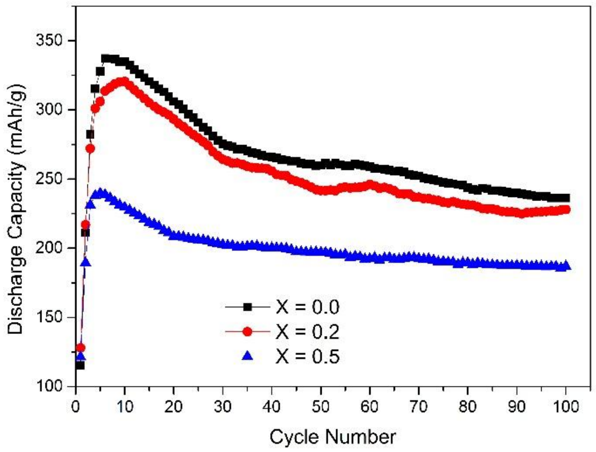

Figure 2 - The cyclic stability of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5) alloys.

The discharge capacity retentions of the alloy electrodes after 100 charge-discharge cycle, C_{100}/C_{max}, are also listed in Table 2, where C_{100} is the discharge capacity of the 100th cycle. It can be seen from Table 2 that the discharge capacity retention of the electrodes alloys increase from 70.2% (x = 0.0) to 78.0% (x = 0.5) after 100th charge-discharge cycles. The pulverization of the alloy particles during the electrochemical tests may be the main hydrogen storage capacity of efficacy loss of the alloy electrode. The oxidation and corrosion layer increased resistance for hydrogen adsorption and desorption during the pulverization of the alloy in alkaline electrolyte. We have also considered that the consequences of oxidation and corrosion layers created a barrier of diffusion of hydrogen atoms in the alloy electrode and decreased drastically property of hydrogen absorption and desorption during the charge-discharge cycles. Therefore, it can be concluded that increase of Sn content in the alloy the corrosion and pulverization resistance of the alloys increase. As put forward by Lin et al. [9] the evidences of increase the cycle life was explained by formation of a passive SnO_2 layer on the surface of the alloy particles preventing the pulverization of electrode materials during the cycling

Table 2 - Electrochemical properties of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5) alloys.

Sample	C_{max} (mAh g^{-1})	C_{100}/C_{max} (%)	$HRD_{1400}(\%)^a$
X = 0.0	337.1	70.2	68.4
X = 0.2	320.5	72.1	36.2
X = 0.5	239.8	78.0	25.7

[a] The high rate dischargeability at a current density of 1400 mA g^{-1}.

CONCLUSIONS

This paper has investigated the influence on a substitution of cobalt by tin on the microstructure and electrochemical properties of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}$ (x = 0.0, 0.2 and 0.5) hydrogen storage alloys. The increasing substitution of Sn for Co resulted in the increase of LaNiSn phase content and the decrease of $LaNi_5$ phase content. When substituted amount of Sn for Co increased from x = 0 to x = 0.5, the electrochemical measurements show that the maximum discharge capacity decreased from 337.1 mAh/g to 239.8 mAh/g; the discharge capacity retention at 100th cycle increased from 70.2% to 78.0%; at a discharge current density of 1400 mA/g.

ACKNOWLEDGEMENTS

The authors wish to thank Institute Nuclear and Energy Research - (IPEN), University of São Paulo for the financial support and thanks are also given to National Council for Scientific and Technological Development – CNPq – Brazil.

REFERENCES

[1] FENG, F.; GENG, M.; NORTHWOOD, D. O. Electrochemical behaviour of intermetallic-based metal hydrides used in Ni/metal hydride (MH) batteries: a review. ***Int. Hydrogen Energy***, v. 26, p. 725, 2001.

[2] FERREIRA, E. A.; SERRA, J. M.; CASINI, J. C.; TAKIISHI, H.; FARIA, R. N. Microstructure and electrochemical properties of a LaMgAlMnCoNi based alloy for Ni/MH batteries. ***Mater. Science Forum***, v. 80, p. 727-728, 2012.

[3] BROWMAN, R. C.; LUO, C. H.; AHN, C. C.; WITHAM, C. K.; FULTZ, B.; The effect of tin on the degradation of $LaNi_{5-y}Sn_y$ metal hydrides during thermal cycling. ***Journal Alloys Compd.***, v. 185, p. 217, 1995.

[4] LAMBERT, S. W.; CHANDRA, D.; CATHEY, W. N.; LYNCH, F. E.; BOWMAN, R. C. Investigation of hydriding properties of $LaNi_{4.8}Sn_{0.2}$, $LaNi_{4.27}Sn_{0.24}$ and $La_{0.9}Gd_{0.1}Ni_5$ after thermal cycling and aging. ***Journal Alloys Compd.***, v. 187, p. 113, 1992.

[5] KUMAR, M. P.; ZHANG, W.; PETROV, K.; ROSTAMI, A.; SRINIVASAN, ADZIC, G. D.; JOHNSON, J. R.; REILLY, J. J.; Effect of Ce, Co, and Sn substitution on gas phase and electrochemical hydriding/dehydriding properties of $LaNi_5$. ***Journal Electrochem. Soc.***, v. 142, p. 3424, 1995.

[6] ZHANG, P.; YONGNING, L.; ZHU, J.; WEI, X.; YU, G. Effect of Al and W substitution for Ni on the microstructure and electrochemical properties of $La_{1.3}CaMg_{0.7}Ni_{9-x}(Al_{0.5}W_{0.5})_x$ hydrogen storage alloys. ***Int. J. Hydrogen Energy***, v. 32, p. 2488, 2007.

[7] REN, J.; ZHANG, Y.; FENG, M.; WANG, G.; ZHAO, X.; WANG, X. Microstructures and electrochemical properties of cobalt-free $LaNi_{4.0}Al_{0.2}Fe_{0.4}Cu_{0.4-x}Sn_x$ (x = 0 - 0.4) electrode alloys prepared by casting. ***Journal Rare Earths***, v. 24, p. 574, 2006.

[8] MA, J.; PAN, H.; CHEN, C.; WANG, Q. The electrochemical properties of Co-free AB_5 type $Ml_{(4.45-x)}Mn_{0.4}Al_{0.15}Sn_x$ hydride electrode alloys. ***Journal Alloys Compd.***, v. 164, p. 343, 2002.

[9] LIN, Q.; ZHAO, S.; ZHU, D.; SONG, B.; MEI, Z. Investigation of hydriding properties and structure of $MlNi_{5-x}Sn_x$ system. ***Journal Alloys Compd.,*** v. 91, p. 351, 2003.