DISCHARGE CAPACITY AND MICROSTRUCTURES OF LaMgPrAlMnCoNi ALLOYS FOR NICKEL-METAL HYDRIDE BATTERIES

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ABSTRACT

$La_{0.7-x}Mg_xPr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ (x = 0.0, 0.3 and 0.7) alloys have been investigated aiming the production of negative electrodes for nickel-metal hydride batteries. The alloys employed in this work were used in the as cast state. The results showed that the substitution of magnesium by lanthanum increased the discharge capacity of the Ni-MH batteries. A battery produced with the $La_{0.4}Mg_{0.3}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy shown a high discharge capacity (380mAh/g) also good stability compared to other alloys. The electrode materials were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Keywords: Ni-MH batteries, hydrogen storage alloys, La-Mg based metal hydrides.

INTRODUCTION

Hydrogen storage alloys has been extensively studied due their potential as negative electrode material in Ni-MH batteries. The importance of these alloys at the performance of the Ni-MH batteries is based on the high capacity, high resistance to overcharging and overdischarging, capacity of performing a high rate charge/discharge and interchangeable with a nickel–cadmium battery. The composition of the hydrogen storage alloy influences directly on the Ni-MH battery characteristics and the La–Mg–Ni system is very promising(1). Recently, it has been reported that in the as-cast condition a $La_{0.7}Mg_{0.3}Al_{0.2}Mn_{0.1}Co_{0.75}Ni_{2.45}$ alloy electrode showed a maximum discharge capacity of 351 mAh/g with good cycling stability(2). R–Mg–Ni (R = rare-earth) type hydrogen storage alloys with the general formula RMg_2Ni_9 have attracted attention widely because of their high hydrogen storage capacity and good electrode properties(3). La-Mg-Ni alloys

have been extensively studied due to its higher discharge capacity ($La_{0.67}Mg_{0.33}Ni_{2.5}Co_{0.5}$) and excellent activation[4] and before of annealing treatment this properties increase[2,4].

EXPERIMENTAL

The alloys were acquired by Less Commom Metals and Wavelength dispersive X-ray fluorescence spectrometer (Rigaku Co., model RIX 3000) was used for elemental determination. In order to prepare the battery the following procedure was adopted. Five grams of the cast alloy was crushed with a mortar and pestle in air and such that all the material passed through a < 44 μm sieve. The negative electrode was prepared using 140 mg of the powder blended with carbon black (67%) and PTFE (33%). Separator and positive electrode ($Ni(OH)_2$) were taken from a commercial battery. This mixture was manually pressed in a form electrode (~2 cm^2 and 1 mm thick). At the charge/discharge cycle tests, charge density adopted in this work was $100mAhg^{-1}$ and discharge density at $50mAhg^{-1}$ until voltage reached 0.9 V. Samples for the microstructure studies were prepared using conventional metallographic methods. The microstructures of the specimens were examined using a scanning electron microscope with energy dispersive X-ray analysis facility. Powdered samples of the alloys (<45 μm) were examined by X-ray diffraction (XRD). Identification of the various phases was carried out by comparison with standards of the ICDD data base and using the software Crystallographica Search-Match (CSM).

RESULTS AND DISCUSSION

The Tab.I shown X-ray fluorescence analysis of $La_{0.7-x}Mg_xPr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ (x = 0.0, 0.3 and 0.7) commercial alloys.

Tab.I – X-ray fluorescence of the alloys.

X	Composition (% wt)						
	La	Mg	Pr	Al	Mn	Co	Ni
0.0	22.9±0.5	-	8.7±0.5	1.6±0.5	5.2±0.5	6.4±0.5	55.1±0.5
0.3	13.1±0.5	2.7±0.5	10.5±0.5	2.2±0.5	6.8±0.5	7.3±0.5	57.0±0.5
0.7	-	4.7±0.5	13.2±0.5	1.7±0.5	6.3±0.5	7.6±0.5	66.5±0.5

Backscattered electron micrographs showing a general view and details of the as-cast alloys are shown in Fig. 1-3. The $La_{0.7}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy is composed of three phases: the major phase (M) and a gray phase (G) and dark gray phase (DG). The others alloys are composed of four phases: M, G, DG and a dark phase (D). The proportion of these four phases in the alloys changed as Mg was included and also as its content increased as showed in Tab. II – V.

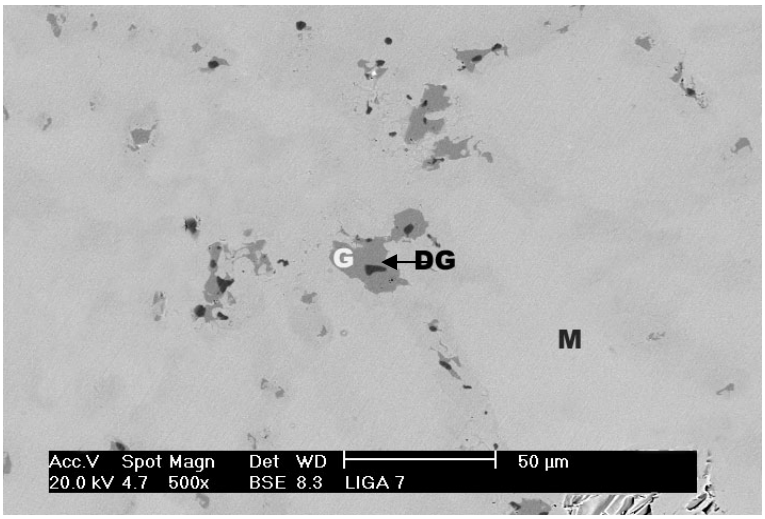

Fig. 1 - Backscattered electron micrograph of the $La_{0.7}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy.

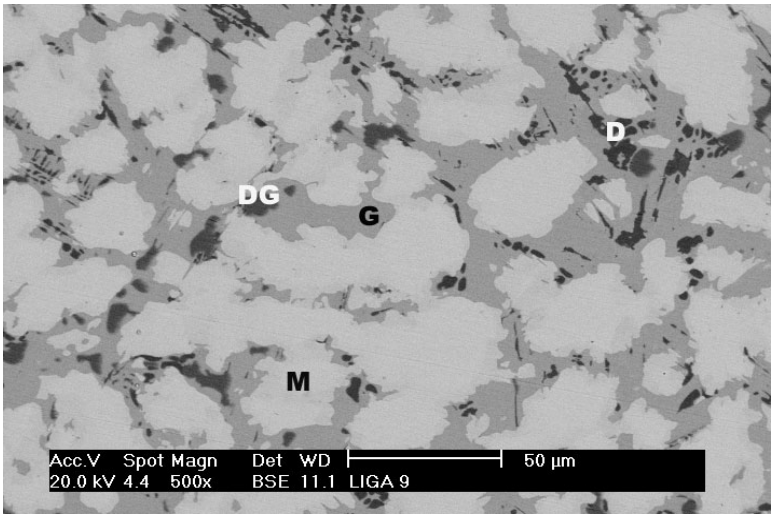

Fig. 2 - Backscattered electron micrograph of the $La_{0.4}Mg_{0.3}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy.

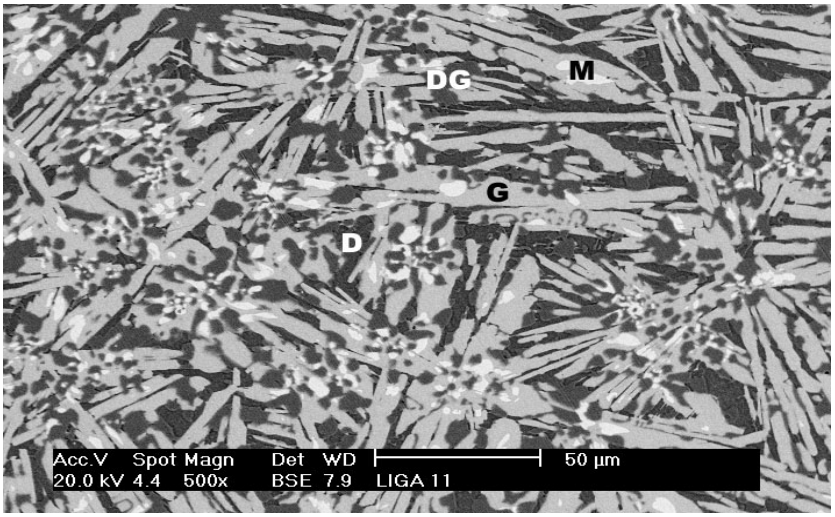

Fig. 3 - Backscattered electron micrograph of the $Mg_{0.7}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy.

Tab. II. Composition determined by EDX at the centers of the M phase.

	Analyzed composition (at.%)							
X	La	Mg	Pr	Al	Mn	Co	Ni	Ratio*
0.0	14.2±0.3	-	4.4±0.3	5.8±0.1	8.5±0.3	7.1±0.5	60.1±0.3	1 : 4.3
0.3	8.8±0.2	-	7.4±0.4	4.3±0.4	3.1±0.7	8.1±0.2	68.3±1.3	1 : 5.1
0.7	-	1.1±0.7	16.8±0.2	2.7±0.2	2.2±0.5	7.3±0.1	69.9±0.6	1 : 4.9

*(La,Pr) : (Mn,Al,Co,Ni)

Tab. III. Composition determined by EDX at the centers of the G phase.

	Analyzed composition (at.%)							
X	La	Mg	Pr	Al	Mn	Co	Ni	Ratio*
0.0	8.8±0.3	-	1.7±0.1	5.4±0.2	23.8±0.7	8.8±0.2	51.5±0.7	1 : 9
0.3	5.4±0.2	10.5±0.4	4.8±0.2	3.4±0.3	6.7±0.2	7.5±0.4	61.7±1.5	1 : 3.8
0.7	-	10.5±0.4	10.6±0.4	2.1±0.1	3.7±0.3	5.6±0.4	67.5±0.3	1 : 3.7

*(La,Pr,Mg) : (Mn,Al,Co,Ni)

Tab. IV. Composition determined by EDX at the centers of the DG phase.

	Analyzed composition (at.%)						
X	La	Mg	Pr	Al	Mn	Co	Ni
0.0	<1	-	<1	9.5±0.3	35.9±1.3	6.7±0.4	47.2±0.7
0.3	<1	<1	<1	10.4±0.5	16.1±0.5	16.1±0.5	56.7±0.9
0.7	-	1.4±0.2	<1	8.9±0.4	11.3±0.4	13.2±0.5	65.2±0.3

Tab. V. Composition determined by EDX at the centers of the D phase.

	Analyzed composition (at.%)							
X	La	Mg	Pr	Al	Mn	Co	Ni	Ratio*
0.0	-	-	-	-	-	-	-	-
0.3	<1	17.7±0.2	<1	3.9±0.3	13.8±0.6	7.3±0.1	56.5±0.3	1 : 4
0.7	-	21.2±0.1	<1	1.7±0.3	8.6±0.2	5.5±0.1	61.5±0.3	1 : 4

*(Mg) : (Mn,Al,Co,Ni)

The chemical compositions showed that for x=0 the M phase is a 1:5-type phase ($LaNi_5$-type) and for x = 0.7 is a ($PrNi_5$-type). The chemical compositions of the G phases showed existence of a R–Mg–Ni phase (*R* = rare-earth) with the general formula RMg_2Ni_9. This phase is very important for Ni-MH batteries due high hydrogen storage capacity and good electrode properties[2,3]. The G phases increase when La is replaced by Mg and becomes the matrix phase for x = 0.7. The DG phases is present in all alloys but in lesser amount for x=0.0. X-ray diffraction patterns of the $La_{0.7-x}Mg_xPr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ of the as-cast alloys are shown in Fig 4. Four phases were identified: $(La,Pr)Ni_5$ (Space group: P6/mmm – PDF: 50-0777), (Al,Mn,Co)Ni (Space group: Fm-3m – PDF: 65-380), $(La,Pr)Mg_2Ni_9$ (Space group: R3m – PDF: 50-1454) and $Mg(Al,Mn,Co)Ni_2$ (Space group: P63/mmc – PDF: 65-3630). Phases G and DG were not identified using X-ray diffraction for x = 0.0 due to the small amount of these phases in the alloy.

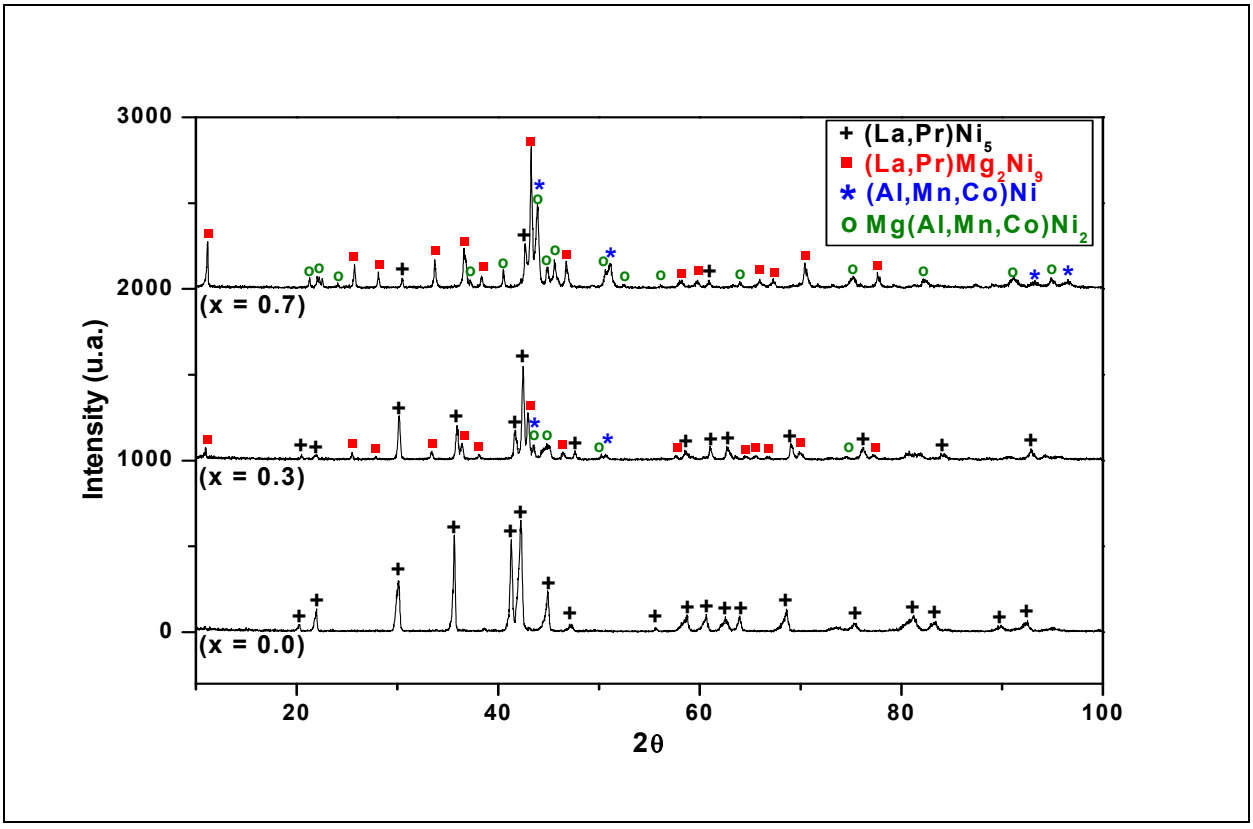

Fig 4 - X-ray diffraction of the $La_{0.7-x}Mg_xPr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ (x= 0.0, 0.3 and 0.7) as-cast alloys.

Cycle life curves and discharge profiles of the negative electrodes prepared using the crushed $La_{0.7-x}Mg_xPr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ as-cast alloys are shown in Fig.5 (a) and (b), respectively. Best performance obtained was $La_{0.4}Mg_{0.3}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy with discharge capacity of 380 mAh/g with good cycling stability. The $Mg_{0.7}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy showed a superior discharge capacity and this has been attributed to a higher amount of the gray phase (G) in this electrode alloy. A short life cycle has been attributed to the amount of DG phase.

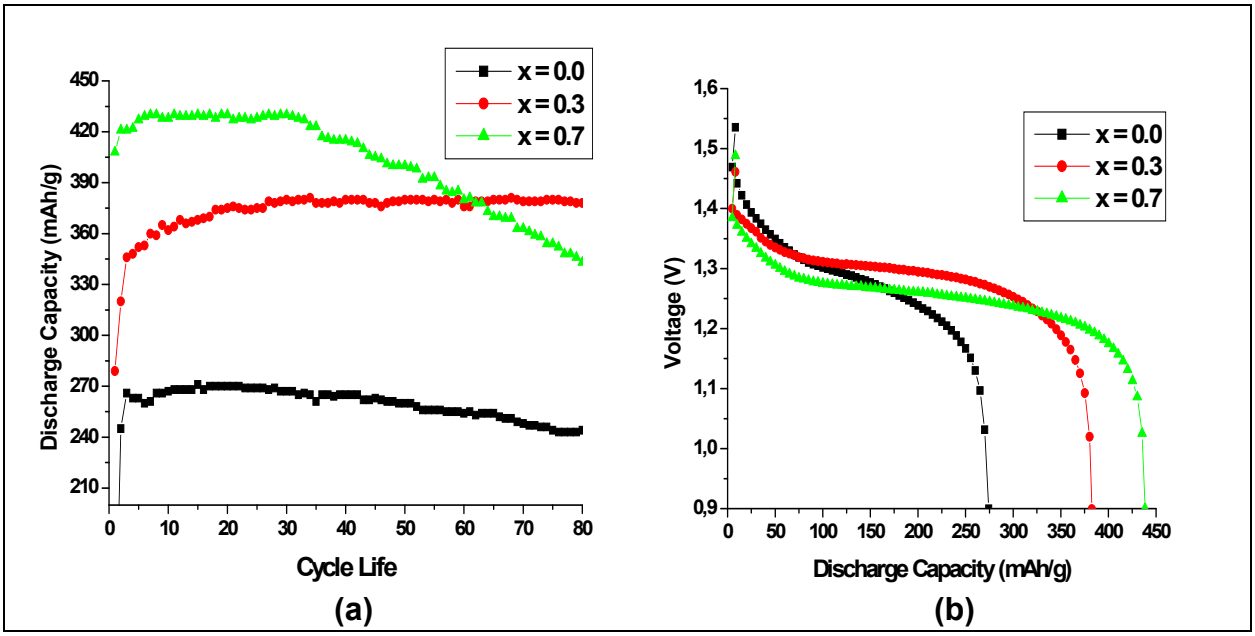

Fig. 5 (a) - cycle life of negative electrode as-cast alloys, (b) discharge profiles the as-cast alloys.

CONCLUSION

In a nickel metal hydride battery the $La_{0.4}Mg_{0.3}Pr_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ electrode alloy exhibited good performance with a maximum discharge capacity of 380 mAh/g and a number of cycles higher than 150. In this alloy a (La,Pr)Mg_2Ni_9 phase (Grey) was present in higher amount and this favored a greater cycle life. A Dark phase (Mg(Al,Mn,Co)Ni_2) and a Dark Gray phase (Ni) present in the studied alloys revealed to detrimental to the cycle life of the battery electrodes.

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