

Effect of Sn and Cu on corrosion resistance of LaMgAlMnCoNi type alloys

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Abstract. This paper reports the results of investigation carried out to evaluate the corrosion resistance of tin and copper in as-cast alloys represented by two sequences series, first: La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8} (x = 0.0, 0.1, 0.2, 0.3 and 0.5) and second: La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-y}Cu_yNi_{3.8} (y = 0.0, 0.1, 0.2, 0.3 and 0.5). Electrochemical methods, specifically, polarization curves have been employed in this study. The effects of Sn and Cu substitution on the composition of the various phases in the alloys and their corrosion resistance have been studied. The electrochemical results showed that corrosion resistance of the alloys increase firstly with Sn replacement and before with copper. Copper substitution yielded good overall performance of the alloys.

Introduction

Hydrogen storage alloys are being studied because of their potential as effective clean energy storage materials. Specifically, AB₅-type alloys are currently used as active materials in nickel metal hydride (Ni-MH) batteries. Ni-MH batteries have higher energy densities than lead-acid and Ni-Cd batteries, but are relatively more expensive to manufacture given recent increases in material costs, particularly for Ni and Co. It has thus become necessary to develop lower cost alloys by partially or totally replacing Ni or Co with cheaper metals such as Mo, Fe, and Cu. Although such alloys are less expensive, their electrochemical performance is not yet satisfactory. It has therefore become necessary to improve the chemical properties and reduce the cost of the low Co AB₅-type alloys [1–5].

The replacement of elements in LaNi₅-type alloys is the most efficient method to obtain desirable characteristics for negative electrodes of the nickel metal hydride batteries. La and Ni can be replaced by other elements: La by Pr, Mg, Ce, Nd or by mishmetal (Mm) [6-9]; and Ni by Mn, Co, Al, Cu or by Nb [10-12] to improve the hydrogen storage capacity, the stability of the hydride phase or the alloy corrosion resistance.

Previous work by this author has shown the effect of Sn substitution of Co in La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8} alloys. It was found that maximum discharge capacity decrease. However an increase of discharge capacity retention could be observed with substitution of Sn by Co [13]. Other work involved the replacement of Sn for Cu in La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-y}Cu_yNi_{3.8} alloys. It was reported that Cu promotes an increase both on discharge capacity and discharge capacity retention at 100th cycle [14].

The aim of the present study was to evaluate the effect of Sn and Cu substitution on the corrosion resistance of LaNi₅-type alloys compound in 6.0 M potassium hydroxide solution. The alloys was subdivided in two series. The first was Sn substitution for Co and the second was Cu substitution for Sn.

Experimental

The nominal composition of the alloys studied can be represented by the following general formula: La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8} (x = 0.0, 0.1, 0.2, 0.3 and 0.5) and La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-y}Cu_yNi_{3.8} (y = 0.0, 0.1, 0.2, 0.3 and 0.5). The purity of all the elements used was at least 99.9%. The alloys were prepared by induction heating in a water-cooled Cu crucible under an argon atmosphere. The ingots were re-melted twice to achieve homogeneity.

The materials characterization, such powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) of these alloys were reported as previous work [13-14].

In order to characterize corrosion resistance of the tested alloys the polarization tests were carried out. The polarization curves were measured in a standard three-electrode electrochemical cell containing Pt mesh and a mercurous oxide (Hg/HgO/6.0M KOH) as the counter electrode (CE) and the reference electrodes (RE), respectively. The electrochemical behavior was evaluated with Solartron potentiostat (SI1287).

The working electrode was prepared by cold epoxy resin mounting after electric contact was established with copper wire. The surface for exposure to the electrolyte was ground and polished to obtain a 1 μm finishing.

The electrochemical tests were carried out in a 6.0M potassium hydroxide solution (KOH) and at 25 °C. All the reagents used for the test solution preparation were per analytical (p.a.) grade. Firstly, samples of all the alloys were immersed in the 6.0M KOH test solution, and the open circuit potential (OCP) was measured as a function of time. The potentiodynamic polarization curves were obtained with a scanning rate of 5mV/s from cathodic towards anodic direction.

Results and discussion

Figure 1 shown the polarization curves 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, 0.1, 0.2, 0.3 and 0.5) alloys. All the electrodes alloys were tested in 6.0 M potassium hydroxide solution at 25 °C and 5 mV/s. Fig. 2 shown the corrosion potential and corrosion current obtained of Tafel polarization curves. All the results are summarized in Tab. 1. It could be observed that corrosion potential (E_{corr}) trends to anodic values and corrosion current (I_{corr}) also increase 1120 mA/cm² to 3580 mA/cm² with Sn substitution. It occurs a possible formation of a passivation layer that increase the corrosion resistance protection of the alloys in 6.0 M potassium hydroxide solution. As reported before [13], the formation of LaNiSn phase on microstructure of these alloys may be explain the increase of corrosion resistance of the Sn-content alloys.

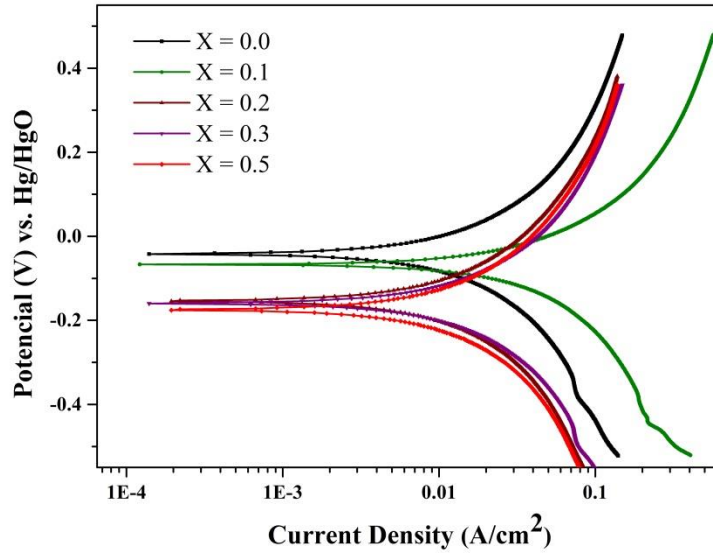


Figure 1. Polarization curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys in 6.0 M potassium hydroxide solution (25 °C, 5 mV/s).

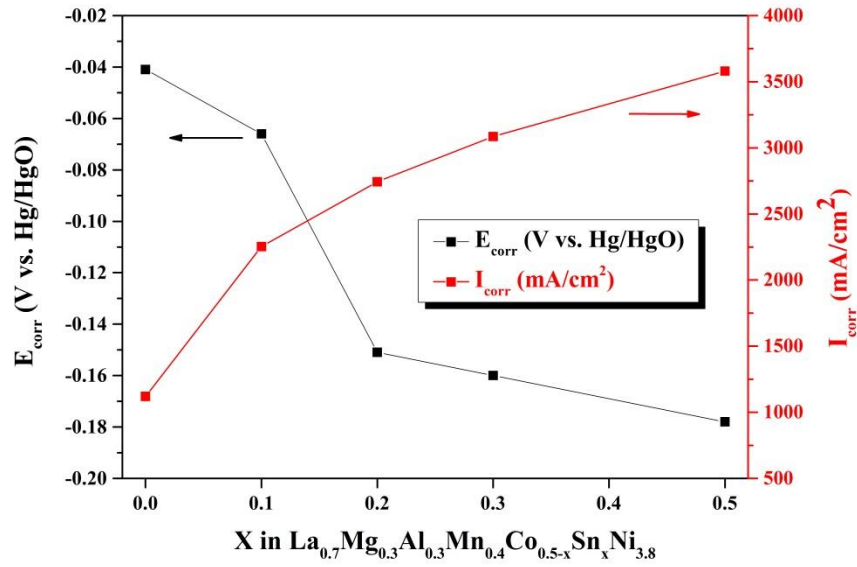


Figure 2. E_{corr} and I_{corr} behavior of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0$ a 0.5) alloys in 6.0 M KOH at 25 °C and 5 mV/s.

Table 1. E_{corr} and I_{corr} of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0$ a 0.5) alloys in 6.0 M KOH at 25 °C and 5 mV/s.

X	E_{corr} (V vs. Hg/HgO)	I_{corr} (mA/cm ²)
0.0	-0.041	1120
0.1	-0.066	2254
0.2	-0.151	2744
0.3	-0.160	3086
0.5	-0.178	3580

Figure 3 shown the polarization curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($y = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys. All the electrodes alloys were tested in 6.0 M potassium hydroxide solution at 25 °C and 5 mV/s. Figure 4 shown the corrosion potential and corrosion current obtained of Tafel polarization curves. All the results are summarized in Table 2. As can be seen the corrosion potential (E_{corr}) trends to more anodic values and corrosion current (I_{corr}) decrease to 3580 mA/cm^2 to 1356 mA/cm^2 with Cu substitution in the alloys. However, in general, the addition of copper makes the alloys less corrosion resistant material (E_{corr} is much more negative with increasing copper content and also I_{corr} is smaller than Sn alloys).

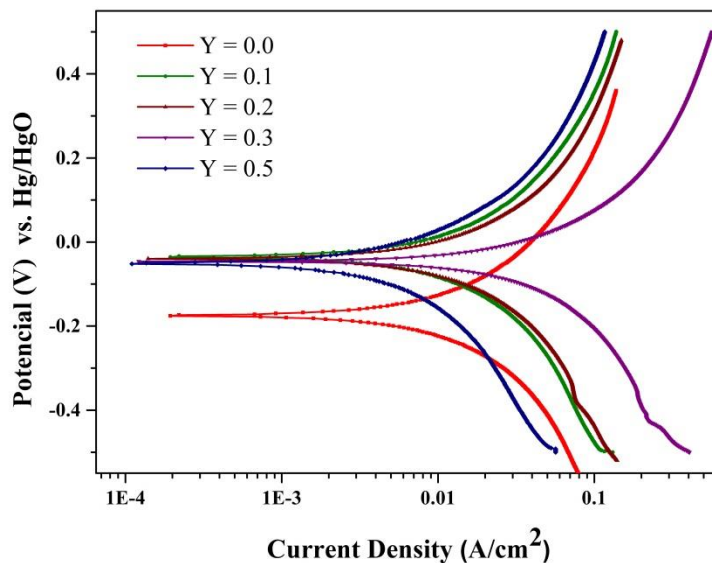


Figure 3. Polarization curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys in 6.0 M potassium hydroxide solution (25 °C, 5 mV/s).

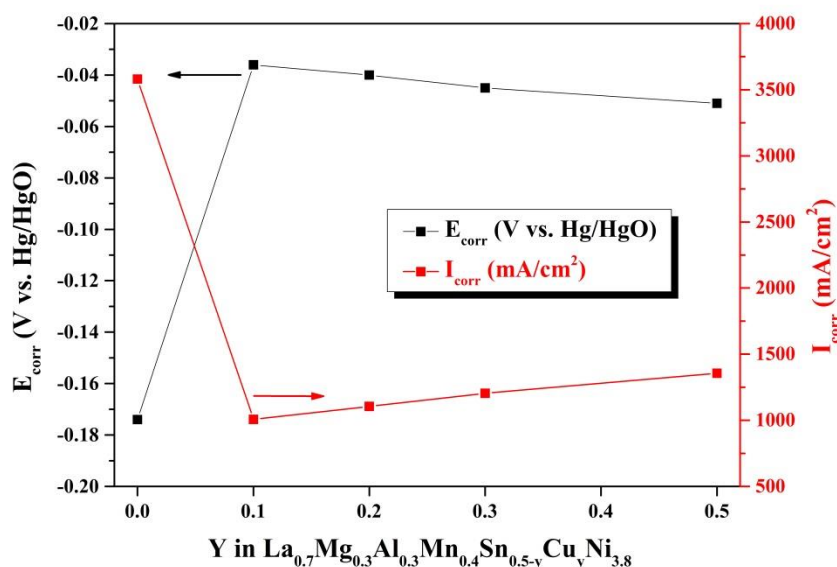


Figure 4. E_{corr} and I_{corr} behavior of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($y = 0.0$ a 0.5) alloys in 6.0 M KOH at 25 °C and 5 mV/s.

Table 2. E_{corr} and I_{corr} of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($y = 0.0$ a 0.5) alloys in 6.0 M KOH at $25\text{ }^\circ\text{C}$ and 5 mV/s .

Y	E_{corr} (V vs. Hg/HgO)	I_{corr} (mA/cm ²)
0.0	-0.174	3580
0.1	-0.036	1007
0.2	-0.040	1104
0.3	-0.045	1204
0.5	-0.051	1356

As reported before [13-14], the results of cyclic stability of the electrodes alloys confirm these results of corrosion resistance. Both Sn and Cu increase the cyclic stability in comparison of Co. However, Cu substitution yields an alloy with a better cyclic stability than Sn. It can be concluded that the corrosion resistance is not the only mechanisms that directly affect the increased of cyclic stability of the electrodes.

Conclusions

This paper has shown that substituting of Sn and Cu in as-cast $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.5) and $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($y = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys has substantial effects on the corrosion resistance of the LaNi_5 -type alloys. The tested alloys show very promising corrosion behavior in strong alkaline solution (6.0 M KOH). The complete substitution of Co for Sn ($\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5}\text{Ni}_{3.8}$ alloys) showiest the best corrosion resistance behavior, and the substitution of Cu by Sn decrease the corrosion resistance. Both elements Sn and Cu shown better corrosion resistance behavior in comparison of Co.

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