

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 sequential 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. 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 Co substitution by Sn 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 Co by Sn [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 compound in 6.0 M potassium hydroxide solution. The alloys was subdivided in two series. The first was Co substitution by Sn and the second was Sn substitution by Cu.

Experimental

The nominal composition of the alloys can be represented by the following general formula: $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ 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). The purity of all the elements 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 reported as previous work [13-14].

In order to characterize the corrosion resistance of the 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 has been grounded 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

Fig. 1 shows the 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. All the electrodes alloys were tested in 6.0 M potassium hydroxide solution at 25 °C and 5 mV/s. Fig. 2 shows 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}) tends to anodic values and corrosion current (I_{corr}) also increase 1120 mA/cm² to 3580 mA/cm² with Sn substitution. This indicates a higher corrosion rate and lower corrosion resistance in the Sn-substituted alloys. As reported before [13], the formation of LaNiSn phase on microstructure of these alloys may explain the lower corrosion resistance of the Sn-content alloys.

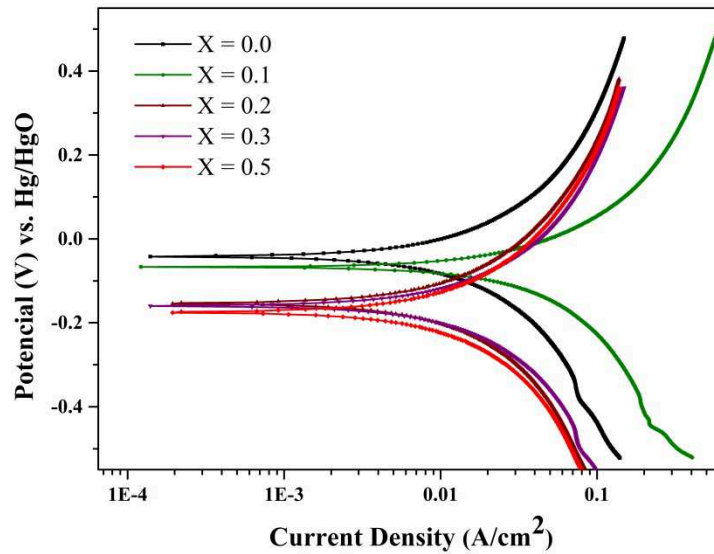


Fig. 1. Polarization curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys in 6.0 M potassium hydroxide solution (25 °C, 5 mV/s).

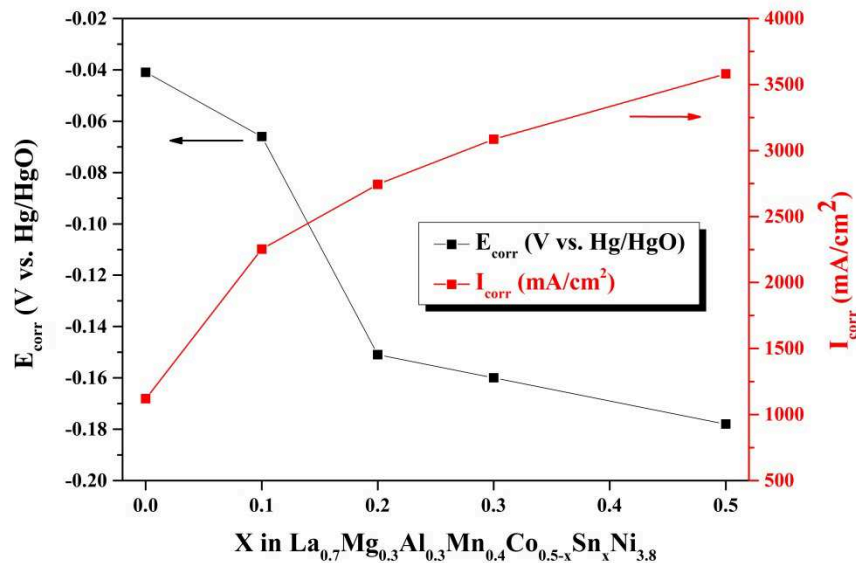


Fig. 2. E_{corr} and I_{corr} behavior of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5-x}\text{Sn}_x\text{Ni}_{3.8}$ ($x = 0.0$ a 0.5) alloys in 6.0 M KOH at 25 °C and 5 mV/s.

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

Fig. 3 shows 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 shows 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}) tends to less anodic values and corrosion current (I_{corr}) decrease to 3580 mA/cm² to 1356 mA/cm² with Cu substitution in the alloys. However, in general, the addition of copper makes an improvement in corrosion resistance.

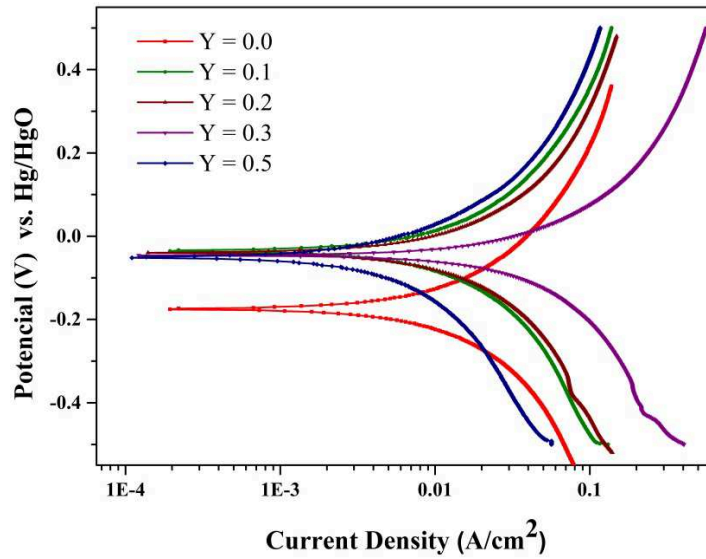


Fig. 3. Polarization curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.5) alloys in 6.0 M potassium hydroxide solution (25 °C, 5 mV/s).

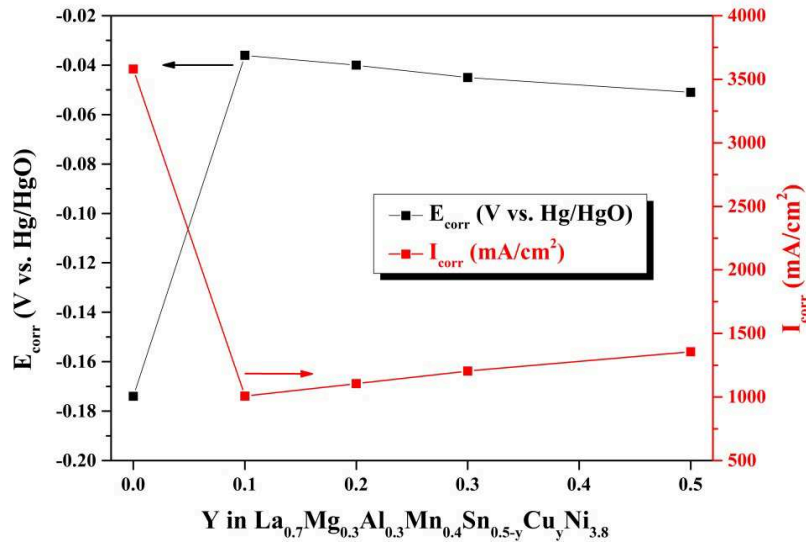


Figure 4. E_{corr} and I_{corr} behavior of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-y}\text{Cu}_y\text{Ni}_{3.8}$ ($y = 0.0$ a 0.5) alloys in 6.0 M KOH at 25 °C and 5 mV/s.

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 °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 [13-15], the results of cyclic stability of the electrodes alloys confirm these results of corrosion resistance. The Cu substituting alloys increase the cyclic stability in comparison with Co and also Cu substitution yields an alloy with a better cyclic stability than Sn [13-15]. It can be concluded that the corrosion resistance is not the only mechanisms that directly affect the increased of cyclic stability of the electrodes. The decrepitation of the alloys during cycling battery charge/discharge better explain the cyclic stability of the alloys in the negative electrodes of Ni-MH batteries than corrosion resistance analyses.

Conclusions

This paper has shown that substituting Co for Sn and/or 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 substitution of elements in the alloys shows different variations corrosion behavior in strong alkaline solution (6.0 M KOH). The $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.4}\text{Cu}_{0.1}\text{Ni}_{3.8}$ alloy shows the best corrosion resistance behavior.

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References

- [1] T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama, H. Ishikawa: *J. Alloy. Compd.* Vol. 180 (1992), 37.
- [2] W. Tang, Y. Gai, H. Zheng: *J. Alloy. Compd.* Vol. 224 (1995), p. 292.
- [3] S. Yang, S. Han, J. Song, Y. Li: *J. Rare Earths* Vol. 29 (2011), p. 692.
- [4] B. Liu, M. Hu, A. Li, B. Zhang, X. Zhu: *J. Rare Earths* Vol. 30 (2012), p. 769.
- [5] J. Ren, T. Zhanga, M. Feng, G. Wang, X. Zhao, X. Wang: *J. Rare Earths* Vol. 24 (2006), p. 574.
- [6] J. Chen, S.X. Dou, H.K. Liu: *J. Power Sources* Vol. 63 (1996), p. 267.
- [7] E.A. Ferreira, L.M.C Zarpelon, J.C.S. Casini, H. Takiishi, R.N. Faria: *Materials Science Forum* Vols. 660-661 (2010), p. 133.
- [8] J. Kleperis, G. Wojcik, A. Czerwinski, J. Skowronski, M. Kopczyk, M. Beltowska-Brzezinska: *J. Solid State Electrochem.* Vol. 5 (2001), p. 229.
- [9] H. Pan, S. Ma, J. Shen, J. Tan, J. Deng, M. Gao: *International Journal of Hydrogen Energy* Vol. 32 (2007), p. 2949.
- [10] Y. Liu, Y. Cao, L. Huang, M. Gao, H. Pan: *J. Alloy. Compd.* Vol. 509 (2011), p. 675.
- [11] T. Huang, Z. Wu, J. Han, G. Sun, J. Yu, X. Cao, N. Xu, Y. Zhang: *Int. J. Hydrog. Energy* Vol. 35 (2010), p. 8592.
- [12] E.A. Ferreira, J.M. Serra, J.C.S. Casini, H. Takiishi, R.N. Faria: *Mater. Sci. Forum* Vols. 727-728 (2012), p. 80.
- [13] J.C.S. Casini, Z.P. Guo, H.K. Liu, E.A. Ferreira, R.N. Faria, H. Takiishi: *Transactions of Nonferrous Metals Society of China* Vol. 25 (2015), p. 520.
- [14] J.C.S. Casini, Z.P. Guo, H.K. Liu, R.N. Faria, H. Takiishi: *Batteries* Vol. 1 (2015), p. 3.
- [15] J.C.S. Casini, F. Martins, Z.P. Guo, H.K. Liu, R.N. Faria, H. Takiishi: *International Journal of Hydrogen Energy* Vol. 1 (2016), p. 17022.