ELSEVIER

Journal of Alloys and Compounds 293–295 (1999) 684–686

Journal of ALLOYS AND COMPOUNDS

Effects of the amount of Mg impurity on the electrochemical properties of Ml(NiCoMnTi)$_5$ hydrogen storage alloy

L.X. Chen[a,*], Y.Q. Lei[a], G.M. Zhu[b], H.G. Pan[a], K. Ren[a], Z.Z. Li[c], X.G. Yang[a], Q.D. Wang[a]

[a]*Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China*
[b]*Department of Chemistry, Xiamen University, Xiamen 361005, PR China*
[c]*Basic Department, Shijiazhuang Machinery Engineering College, Shijiazhuang 050003, PR China*

Abstract

For the purpose of scientific control of the content of magnesium impurity in hydrogen storage electrode alloys during industrial production, the effects of magnesium content on electrochemical performances of a mischmetal based alloy Ml(NiCoMnTi)$_5$ has been investigated by doping the alloy with various amounts of magnesium intentionally. The electrochemical measurement shows that the discharge capacity increases slightly from 302 to 315 mAh/g as the magnesium content in the alloy increases from 0.003 to 0.263%. However, when the magnesium content increases further, the capacity starts to decrease gradually. As the magnesium content increases, the activation behavior and high-rate-dischargeability are enhanced to some degree, but the self-discharge (24 h) of the electrode rises greatly. It is found that the cycling stability deteriorates rapidly as the magnesium content increases beyond 0.100%. Therefore, it is appropriate to control the content of magnesium impurity in the Ml(NiCoMnTi)$_5$ alloy under 0.100%.

Keywords: Magnesium impurity; Hydrogen storage alloy; Electrochemical properties

1. Introduction

Owing to their excellent performance/cost ratio, mischmetal-based AB$_5$-type hydrogen storage electrode alloys have been widely used as the negative electrode materials of Ni/MH batteries. In industry production, the A-side composition of the alloy is generally that of commercial mischmetal, and the B-side composition is Ni and its partial substitutional elements (e.g. Mn, Co, Ti, Al etc.) [1–6]. However, the content of impurities (e.g. Mg, Fe, Si etc.) in commercial mischmetal is different for different ores and extraction methods [4–8]. At the same time, in the melting process of the alloy, owing to the interaction between the high temperature melting flux and the melting crucible or water-cooled steel mold, the alloy will be contaminated by tiny amount of Mg and other elements, called the doping elements hereafter, which may have a substantial influence on the electrochemical properties of the alloys. On account of this effect, for the purpose of controlling the content of magnesium impurity in hydrogen storage electrode alloys during industry production on a scientific basis, the effects of magnesium content on electrochemical performances of mischmetal based alloy Ml(NiCoMnTi)$_5$ (Ml: La-rich mischmetal) [1] have been investigated by doping the alloy with various amounts of magnesium intentionally.

2. Experimental

The alloy-samples were prepared by arc furnace melting under an argon atmosphere in a water-cooled copper crucible. The purity of raw materials were: mischmetal (Ml) 99.32% (containing: 64.60% La, 5.89% Ce, 26.56% Pr, 2.23% Nd, 0.10% Mg, 0.36% Fe, 0.02% Si), Ni 99.95%, Co 99.5%, Mn 99.7%, Ti 99.5% and Mg 99.8%. Eight alloy-samples with the following Mg content were prepared separately namely 0.003%, 0.100%, 0.156%, 0.217%, 0.263%, 0.353%, 1.030% and 1.090% as determined by ICP analysis. The doped-alloys were ground into powders of 74–33 μm (200–500 mesh), and mixed with Cu powder in the weight ratio of 1:2, then pressed to form round-disc electrodes of 10 mm diameter (about 100 mg hydrogen storage alloy per pellet). Each electrode

*Corresponding author. Fax: +86-571-795-1152.
E-mail address: leiyq@sun.zju.edu.cn (L.X. Chen)

0925-8388/99/$ – see front matter
PII: S0925-8388(99)00431-4

pellet was tested at 25°C in an open-cell with an electrolyte of KOH (6 mol/l), a positive electrode of $Ni(OH)_2$/NiOOH and a reference electrode of Hg/HgO/KOH (6 mol/l). The discharge capacity, activation behavior, high-rate-dischargeability, self-discharge and cycling stability of the doped-alloys were tested respectively under following conditions:

1. For activation behavior and discharge capacity measurements, charging at 60 mA/g for 7.5 h and discharging at 60 mA/g to the end point.
2. For high-rate-dischargeability measurement, charging at 60 mA/g for 7.5 h and discharging at 300 mA/g to the end point.
3. For self-discharge (24 h) measurement, charging at 60 mA/g for 7.5 h, then discharging at 60 mA/g after 24 h.
4. For cycling stability measurement, charging at 300 mA/g for 1.2 h and discharging at 300 mA/g per cycle, and measuring the discharge capacity after every 50 cycles.

The end point of the discharge was set to −0.6 V (versus Hg/HgO).

3. Results and discussion

The relationship between the content of doping Mg and the discharge capacity of the doped-alloys are shown in Table 1. It can be seen from Table 1 that the discharge capacity is improved from 302 to 315 mAh/g as the Mg content in the alloy increases from 0.003 to 0.263%. However, when the content of doping Mg increases further, the discharge capacity decreases gradually, for example, the maximum capacity of the alloy with 1.090% Mg content is 304 mAh/g.

The activation behavior of the doped-alloys is shown in Fig. 1, from which it can be seen that as the Mg content in the alloy increases, the activation behavior is improved, and the activation cycle number decreases. For example, the activation cycle number is five when the Mg content is

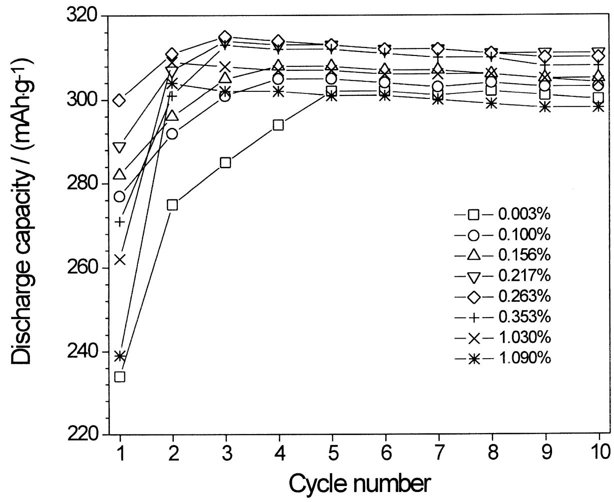

Fig. 1. Activation behavior of the doped-alloys with various amount of Mg.

0.003%, and the activation cycle number is only two when the content of doped Mg=1.030%.

The high-rate-dischargeability ($C_{300\ mA}/C_{60\ mA}$) of the doped-alloys in Table 1 shows that moderate content of Mg can enhance the high-rate-dischargeability of the alloy to some degree. When the Mg content increases from 0.003 to 1.030%, the high-rate-dischargeability increases from 78.50 to 87.38%, and when the Mg content increases further, the high-rate-dischargeability decreases slightly.

Self-discharge characteristics (24 h) of the doped-alloys in terms of the charge retention versus the Mg content in the alloy is shown in Fig. 2, from which it can be seen that the capacity retention drops rapidly from 93.47 to 66.71% as the Mg content increases from 0.003 to 0.353%. However, when the Mg content increases further, the rate of the capacity retention is still decreasing but rather slowly.

Fig. 3 indicates the cycle life curves of doped-alloys. As shown in Fig. 3, the capacity-decay rate of the original alloy (i.e. 0.003% Mg) is smaller than others, with its maximum capacity equaling 302 mAh/g and capacity retention after 200 cycles equaling 82.50%. When the Mg content in the alloy exceeds 0.100%, the decay rate increases rapidly. For example, as the Mg content is

Table 1
Electrochemical properties of the doped-alloys with various amount of Mg

Mg content (wt.%)	Discharge capacity $C_{60\ mA}$ (mAh/g)	Activation cycle number	High-rate-dischargeability $C_{300\ mA}/C_{60\ mA}$ (%)
0.003	302	5	78.50
0.100	305	4	78.69
0.156	308	4	79.22
0.217	314	3	80.57
0.263	315	3	82.86
0.353	313	3	84.35
1.030	309	2	87.38
1.090	304	2	85.86

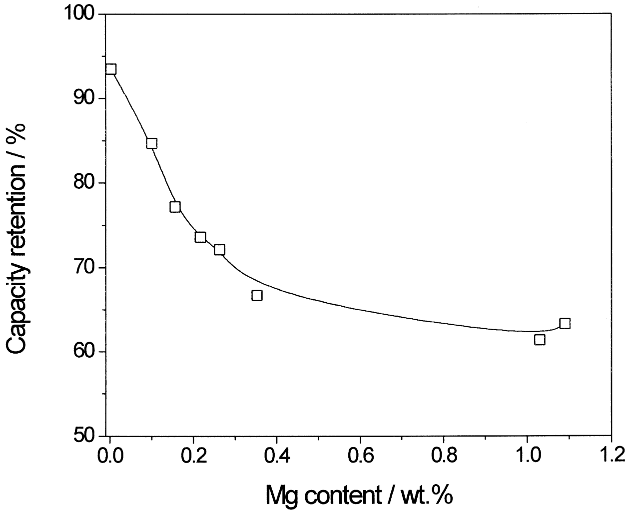

Fig. 2. Self-discharge (24 h) of doped-alloys with various amount of Mg.

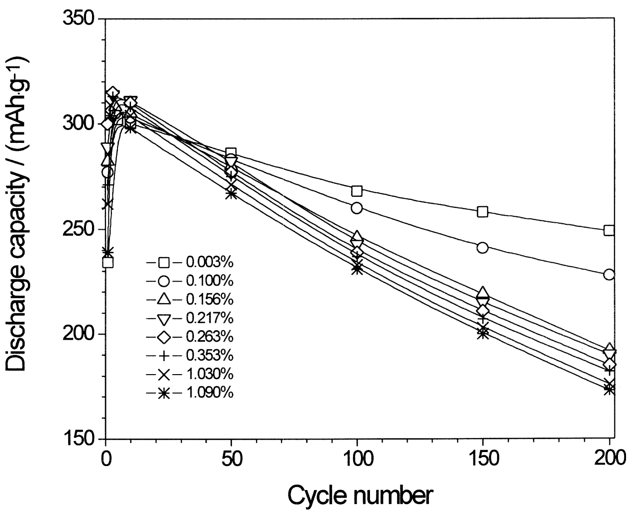

Fig. 3. Cycle life curves of doped-alloys with various amount of Mg.

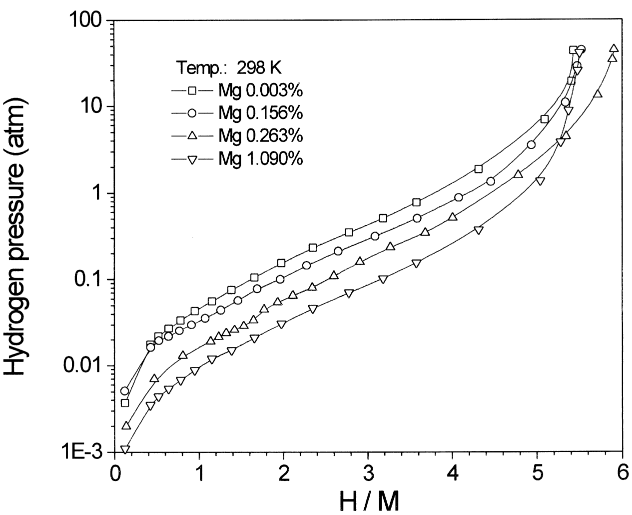

Fig. 4. *P–C–T* curves of four doped-alloys at 298 K.

1.090%, its capacity retention after 200 cycles drops to 56.89%. So the cycling stability of the alloy is unsatisfactory as the Mg content in the alloy is above 0.100%.

The pressure–concentration isotherms of four doped-alloys (with Mg content: 0.003%, 0.156%, 0.263%, 1.090%) at 25°C are shown in Fig. 4. It is found that the pressure plateau of the alloy with 0.263% Mg content is wider than others, and the equilibrium plateau pressure drops gradually when the Mg content in the alloy increases.

4. Conclusions

The electrochemical measurements show that the electrochemical performances of the $Ml(NiCoMnTi)_5$ alloy, including discharge capacity, activation behavior, high-rate-dischargeability, charge-retention and cycling stability, are influenced distinctly by the content of magnesium impurity in the alloy. From our experiments, it is appropriate to control the content of magnesium impurity in the $Ml(NiCoMnTi)_5$ alloy to around 0.100 wt.%.

Acknowledgements

Financial support by the National Advanced Materials Committee of China.

References

[1] Y.Q. Lei, Z.P. Li, J. Wu, Q.D. Wang, J. Less-common Met. 172 (1991) 1265.
[2] F. Meli, A. Zuettel, L. Schlapbach, J. Alloys Comp. 202 (1993) 81.
[3] K. Suzuki, N. Yanagihara, H. Kawano, A. Ohta, J. Alloys Comp. 192 (1993) 173.
[4] L.X. Chen, Y.Q. Lei, Trans. Nonferrous Met. Soc. China 8 (1998) 256.
[5] L.X. Chen, Y.Q. Lei, Nonferrous Metals 2 (1998) 104.
[6] J.J. Jiang, Y.Q. Lei, D.L. Sun, C.S. Wang, J. Wu, Q.D. Wang, Acata Metallurgica Sinica 31 (1995) B379.
[7] Y.Q. Lei, J.J. Jiang, D.L. Sun, J. Wu, Q.D. Wang, J. Alloys Comp. 231 (1995) 553.
[8] R. Balasubrarnanian, M. IV Mungol, R.N. Rai, J. Alloys Comp. 196 (1993) 63.