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Corrosion mechanism of mechanically alloyed Mg50Ni50 and Mg45Cu5Ni50 alloys^①

ZHANG Yao(张 耀), LI Shou-quan(李寿权), CHEN Li-xin(陈立新),
LEI Yong-quan(雷永泉), WANG Qi-dong(王启东)
(Department of Materials Science and Engineering, Zhejiang University,
Hangzhou 310027, China)

[Abstract] As the loss of active material Mg may affect electrode's discharge capacity and the cycling stability, a more refined mechanism study on cycling capacity degradation should be made. The present investigation is based on the supposition that the capacity degradation of the binary Mg50Ni50 alloy and ternary Mg45Cu5Ni50 alloy electrodes is solely due to the corrosion of Mg, the active hydrogen storage element. That means amount of capacity degradation is determined by the corrosion current time, which is also the time of operation. The corrosion current J_{corr} dependence on cycling time was deduced. A mathematic relation between the cycling capacity retention $C_N / C_1 (\%)$ and the duration of operation was also deduced. The data calculated from the equations deduced agree well with those of the experiment result. The loss of the active hydrogen absorbing element Mg is proved to be the main cause for cycling capacity deterioration in the present investigation.

[Key words] mechanism of degradation; cycling capacity degradation; corrosion current; MgNi based alloys

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1 INTRODUCTION

Magnesium based mechanically alloyed electrode alloys are one kind of the promising hydrogen storage electrode alloys for Ni/MH batteries owing to their large hydrogen capacity, low cost and excellent initial electrochemical activity during the charge and discharge process^[1~3]. But their poor cycling stability hampers their immediate application and even discourages further research and development. Many methods have been tried to overcome the shortage^[4~9], however no great breakthrough has been achieved up to date. Many previous studies have shown that the cycling capacity deterioration is due to the formation and growth of the passive $\text{Mg}(\text{OH})_2$ film over the surface of the alloy^[10], and some capacity deterioration models have been framed^[11, 12]. This $\text{Mg}(\text{OH})_2$ film which is regarded as the corrosion product of Mg in alkaline solution, not only deteriorates the surface activity and increases the electric resistance, but also decreases the Mg content in the alloy and thus leads to the loss of hydrogen storage capacity. All these factors influence the cycling capacity degradation. In order to find out the main cause, we are trying to analyze it quantitatively. In this paper a mathematic relation among the capacity deterioration rate, the corrosion current and the corrosion time is deduced and the calculated deterioration values are compared with the experimental results of the mechanically alloyed binary Mg50Ni50 and ternary

Mg45Cu5Ni50 electrode alloys.

2 EXPERIMENTAL

Mg50Ni50 and Mg45Cu5Ni50 alloys were synthesized by means of mechanical alloying (MA). Metal powders of purity higher than 99.9% were mixed evenly according to stoichiometric ratio, and sealed in vials first evacuated and then filled with pure argon gas. The ball to powder ratio was 30:1. After 120 h ball milling, amorphous alloys were formed. Fig.1 shows the XRD patterns of both alloys ballmilled for 120 h. The alloys powders after being mixed with copper powder in the mass ratio of 1:2

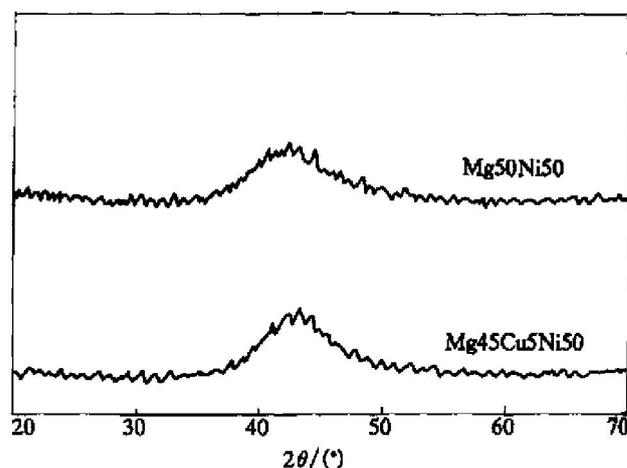


Fig. 1 XRD patterns of mechanical ball milling Mg50Ni50 and Mg45Cu5Ni50 alloys

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were pressed into pellets of 10 mm diameter. The pellets were tested as the working electrode in a tri-electrodes system. The other two electrodes, the counter electrode and the reference electrode, were Ni(OH)₂/NiOOH and Hg/HgO respectively. The charge-discharge cycling was monitored by means of an automatic Galvanostat (DC-5 system). For the charge process the current density of 300 mA/g for 3 h was adopted, while discharge process was conducted at 100 mA/g until the cutoff voltage - 0.6 V (vs Hg/HgO, 6 mol/L KOH) was reached.

The corrosion current was tested on a CH1600A electrochemical analysis workstation by means of linear sweep voltammetry with scanning rate of 0.005 V/s. The disturbing potential (ΔV) was ± 0.01 V over the open circuit potential to make sure the polarization process located at the region of linear polarization. The linear sweep voltammetry was executed from cathodic polarization to anodic polarization. For revealing the variation of J_{corr} with cycling time, we measured the open circuit parameters at the ending moment of each cycle. The initial J_{corr} for the alloy were measured at the moment when open circuit potential was more negative than the corrosion potential of copper (- 0.46 V vs Hg/HgO, 6 mol/L KOH) during the first charge process.

3 RESULTS AND DISCUSSION

3.1 Cycling stability

The dependence of discharge capacity on cycling number of the test alloy is exhibited in Fig. 2. Compared to Mg50Ni50 alloy, Mg45Cu5Ni50 alloy shows a lower initial discharge capacity (365 mA·h/g) but a higher cycling stability (the initial capacity C_1 , discharge capacity after 20 cycles C_{20} and the capacity retention C_{20}/C_1 are listed in Table 1). Its capacity retention after 20 cycles is 58.1%, higher than that of Mg50Ni50 (44.2%). So it shows that the Cu substitution for Mg does help to improve the poor cycle capacity retention.

Table 1 Discharge capacity and cycling retention of Mg50Ni50 and Mg45Cu5Ni50 electrodes

Alloy	C_1 /(mA·h·g ⁻¹)	C_{20} /(mA·h·g ⁻¹)	C_{20}/C_1 /%
Mg50Ni50	464	205	0.442
Mg45Cu5Ni50	365	212	0.581

3.2 Mathematic relation between cycling capacity degradation, corrosion current and cycling time

In a previous study^[12], the growth of passive Mg(OH)₂ film over surface was ascribed as the main cause of cycling capacity degradation. Such a film not only weakens the surface electrocatalytic activity but also represents the amount of the loss of hydrogen absorption of element Mg and hence loss of hydrogen storage capacity. The rate of growth of the passive

Mg(OH)₂ film should be a function of the corrosion current of the alloy and duration of operation. The quantitative relationships between them is as follows.

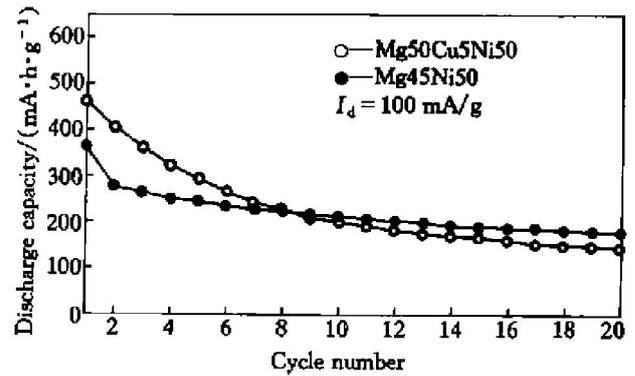


Fig. 2 Dependence of discharge capacity on cycling number of Mg45Cu5Ni50 and Mg50Ni50 prepared by mechanical alloying

According to Stern and Geary^[13], when the system is in the stationary state, the polarization current could be expressed as

$$J = J_{\text{corr}} \left[\exp\left(\frac{\Delta E}{\beta_a}\right) - \exp\left(-\frac{\Delta E}{\beta_c}\right) \right] \quad (1)$$

where ΔE stands for potential deviation from equilibrium state and β_a , β_c are the Tafel slopes for the anodic and cathodic polarization reactions.

In this work, when ΔE is very small, Eqn. (1) could also be simplified as

$$\begin{aligned} J &\approx J_{\text{corr}} \left[1 + \frac{\Delta E}{\beta_a} - \left(1 - \frac{\Delta E}{\beta_c} \right) \right] \\ &= J_{\text{corr}} \left[\frac{\Delta E}{\beta_a} + \frac{\Delta E}{\beta_c} \right] \\ &= J_{\text{corr}} \Delta E \left[\frac{\beta_a + \beta_c}{\beta_a \beta_c} \right] \end{aligned} \quad (2)$$

This is also the disturbed current ΔJ in the linear region for a small voltage disturbance ($\Delta E = 10$ mV):

$$\Delta J = J_{\text{corr}} \Delta E \left(\frac{\beta_a + \beta_c}{\beta_a \beta_c} \right) \quad (3)$$

The polarization resistance R_P under this operation condition is

$$R_P = \Delta E / \Delta J = (1/J_{\text{corr}}) \beta_a \beta_c / (\beta_a + \beta_c) \quad (4)$$

where ΔE and ΔJ are disturbing potential and disturbing current respectively, with

$$\beta_a = \frac{2.303RT}{anF} \quad (5)$$

$$\beta_c = \frac{2.303RT}{(1-a)nF} \quad (6)$$

and J_{corr} is the corrosion current density. We can simplify Eqn. (4) to

$$R_P = K / J_{\text{corr}} \quad (7)$$

Since β_a and β_c are the activation energies for the oxidation and reduction processes respectively, hence are constants in this work. a in Eqns. (5) and (6) denotes the transferring index (here is taken as 1/2). Thus K becomes a constant in the whole reaction.

R_P in this reaction varies with the number of cy-

cling, and can be determined by $\Delta E / \Delta J$, in which ΔE is the small applied potential and ΔJ is the corresponding electric current. Generally $\Delta E - \Delta J$ relation is a straight line, from which R_p can be obtained as its slope. Fig. 3 shows the $\Delta E - \Delta J$ relation of the reaction at the initial charge moment during the first cycle of both alloys. The slopes of this curve are R_p of both electrodes after the first cycle. The same method was used for the subsequent cycles to obtain R_p of the reaction at different cycling times. The tested R_p values are listed in Table 2. With this series of R_p values thus obtained at the end of different cycles, we obtained a series of J_{corr} values varied with number of cycles or duration of operation, which equals the product of number of cycles and time for each cycle in seconds. Thus, the relation between J_{corr} and the corrosion time of Mg50Ni50 and Mg45Cu5Ni50 were shown in Fig. 4 and Fig. 5 respectively, from which, it could be seen that the J_{corr} of both alloys were all decreasing exponentially with the total time of charge and discharge cycles. Through exponential fitting, Eqn. (8) is its mathematic representation:

$$J_{corr}(t) = J_0 \exp(-t/\tau) \quad (8)$$

For Mg50Ni50 and Mg45Cu5Ni50 alloys, J_0

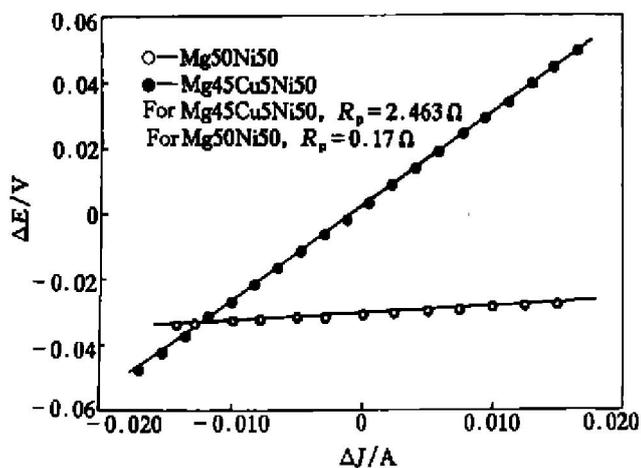


Fig. 3 Linear-polarization curves of Mg50Ni50 and Mg45Cu5Ni50 electrodes at initial cycling line

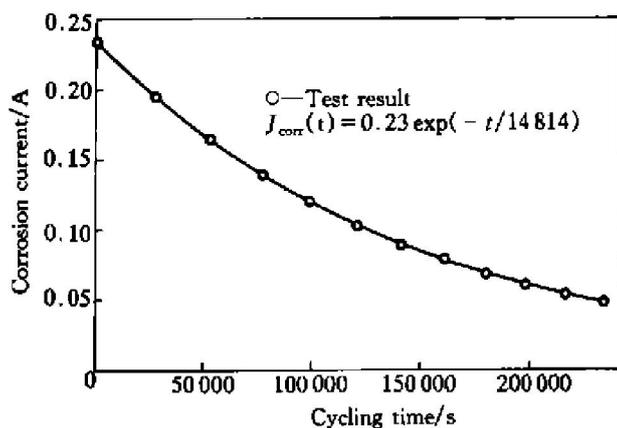


Fig. 4 Relation between J_{corr} and cycling time of Mg50Ni50 electrode

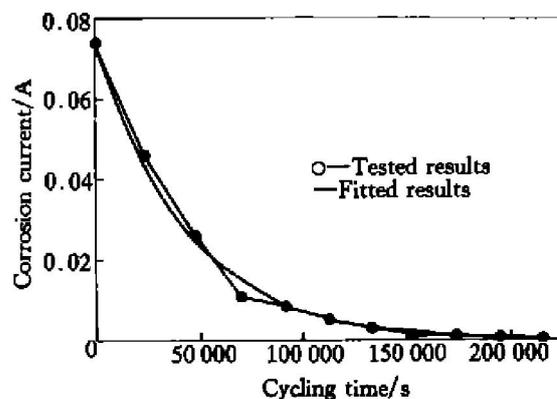


Fig. 5 Relation between corrosion current and cycling time of Mg45Cu5Ni50 electrode

Table 2 Tested R_p values varied with different cycling times

Cycling time / 10^3 s	R_p of Mg50Ni50 / Ω	R_p of Mg50Cu5Ni50 / Ω
0	0.1	2.64
23.5	0.17	4.20
47.7	0.24	7.48
70.2	0.32	17.9
91.5	0.38	23.1
113	0.44	38.9
134	0.5	64.8
155	0.58	129
174	0.65	162
195	0.73	343
215	0.82	343

equals to 0.233 A and 0.0733 A respectively, τ equals to 148141 and 41677 respectively.

According to the Faraday's law, the mass of Mg corroded in a short time interval Δt can be expressed by

$$\Delta m = A J_{corr}(t) \Delta t / nF \quad (9)$$

where A is the atomic mass of Mg, n is the number of transferred electrons per atom, Δt is the corrosion time interval, F is the Faraday constant. Because $J_{corr}(t)$ is a function of corrosion time t , Eqn. (9) should be transformed into the following differential Eqn. (10):

$$dm = \frac{A}{nF} J_{corr}(t) dt \quad (10)$$

On integration, we obtained

$$\Delta m = \frac{A}{nF} \int_{t_1}^{t_1+\Delta t} J_{corr} dt \quad (11)$$

On the supposition of Mg corrosion as mentioned above, the following relation is obtained:

$$D = \frac{C_1 - C_N}{C_1} = \frac{M_1 - M_N}{M_1} = \frac{\Delta M}{M_1} \quad (12)$$

where D means the cycling degradation rate, C_1 and C_N stand for the initial capacity and the capacity after N cycles. M_1 and M_N stands for the initial hydrogen storage alloy mass and that after N cycles.

Therefore,

$$D = \frac{A}{nF} \int_{t_1}^{t_1+\Delta t} J_{corr} dt \quad (13)$$

The cycling capacity retention rate is

$$\frac{C_N}{C_1} = 1 - \frac{A}{nF} \int_{t_1}^{t_1+t} J_{\text{corr}}(t) dt \quad (14)$$

After substituting Eqn. (8) into Eqn. (13) and Eqn. (14) and integrating, we obtain

$$C_N/C_1 = a + b \exp(-t/\tau) \quad (16)$$

For Mg50Ni50 alloy, a , b and τ equal to 0.1027, 0.362 and 148141 respectively. For Mg45Cu5Ni50 alloy, a , b and τ are 0.6116, 0.3884 and 41677 respectively. The equations are expressed in Fig. 6 and Fig. 7.

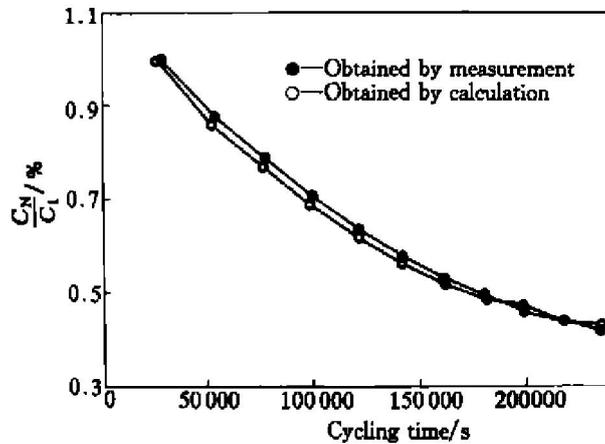


Fig. 6 Comparison of calculated and tested C_N/C_1 varied with cycling time of Mg50Ni50 electrode

3.3 Comparison between deduced and tested results of C_N/C_1

From the equation, the cycling capacity retention rate for the different periods of operation can be calculated. The calculated values agree well with all those obtained by measurements as exhibited in Fig. 5. It indicates that in the duration 69.4 h or 69.0 h, the cycling stability of Mg50Ni50 and Mg45Cu5Ni50 alloy electrodes are determined solely by the corrosion of Mg. We also believe Eqns. (13) and (14) are also applicable for other MA

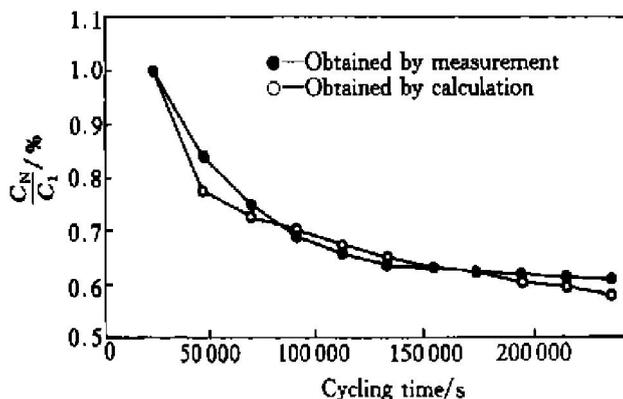


Fig. 7 Comparison of calculated and tested C_N/C_1 varied with cycling time of Mg45Cu5Ni50 electrode

Mg-based alloy electrodes, at least in the early stage of operation, in which the $\text{Mg}(\text{OH})_2$ layer is not thick enough to form a detectable diffusion and resistance over-voltage. This result also leads us to believe that the $\text{Mg}(\text{OH})_2$ surface layer produced in this electrode process is quite porous and permeable to the electrolyte so that no detectable diffusion and resistance over-voltage has been built up in this duration of investigation. Further investigations are to be made for a longer period of operation and also for alloys of lower cycling capacity retention.

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