

Effects of Hg and Ga on microstructures and electrochemical corrosion behaviors of Mg anode alloys

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Received 9 October 2011; accepted 9 September 2012

Abstract: The effects of Hg and Ga on the electrochemical corrosion behaviors of the Mg–2%Hg, Mg–2%Ga and Mg–2%Hg–2%Ga (mass fraction) alloys were investigated by measurements of polarization curves, galvanostatic tests and measurements of electrochemical impedance spectroscopy. Scanning electron microscopy, X-ray diffractometry and energy dispersive spectrometry were employed to characterize the microstructures and the corroded surface of the above alloys. The results demonstrate that the microstructure of the Mg–2%Ga alloy is solid solution and the Mg–2%Hg and Mg–2%Hg–2%Ga alloys have white second-phases at the grain boundaries. The Mg–2%Ga alloy has the worst electrochemical activity and the best corrosion resistance, showing a mean potential of -1.48 V and a corrosion current density of 0.15 mA/cm². The Mg–2%Hg–2%Ga alloy has the best electrochemical activity and the worst corrosion resistance, showing a mean potential of -1.848 V and a corrosion current density of 2.136 mA/cm². The activation mechanism of the Mg–Hg–Ga alloy is dissolution-deposition of the Hg and Ga atoms.

Key words: Mg anode alloy; microstructure; electrochemical activity; corrosion resistance; electrochemical impedance spectroscopy

1 Introduction

Magnesium and its alloys are used extensively as the seawater battery materials and cathodic protection (CP) materials due to their excellent properties such as rapid activation, high power density capability, high electrode potential (-2.37 V vs NHE), light mass and relative abundance in sea-water and earth [1–3]. The developed magnesium anode alloys are AZ system alloy and AP65 [4–6]. However, these commercial magnesium anode alloys have some problems, such as positive mean potential, severe polarization phenomenon and bad deformability, and anode mud sheds difficultly when used in high power seawater battery. So these Mg anode alloys are not fit for high power seawater battery anode materials. In order to search for the good properties of magnesium anode used in high power seawater battery, alloying, a promising way to solve the problems of the positive mean potential, bad deformability and large self-corrosion rate, was proposed [7–9]. Recently, the effects of alloying elements such as aluminum (Al), zinc (Zn), lead (Pb), manganese (Mn) and tin (Sn) on the magnesium anodes have been investigated [10–12]. But

there are no any reports about the chemical composition and processing technology of Mg anode materials used in high power seawater battery.

According to Refs. [13–16], Hg ions deposit on the surface of the anode and form amalgams, which can initiate the activation process, detach the passive film and make the mean potential negative. Ga ions can deposit on the electrode surface to increase the adsorption of Cl⁻ ions and inspire the activation. But the effects of Hg and Ga on the electrochemical activity and the corrosion resistance of Mg anodes were not reported in detail. In this work, Hg and Ga were added into the magnesium anode alloys and the effects of Hg and Ga on the microstructures and the electrochemical properties of the Mg anode alloys were studied.

2 Experimental

The Mg–2%Hg, Mg–2%Ga and Mg–2%Hg–2%Ga alloys were prepared using metal with 99.99% purity in order to avoid contamination by other elements. The alloys were melted in a sealed iron tube filled with Ar atmosphere, and then air cooled. After homogeneous heat treatment at 673 K for 24 h, these alloys were water

cooled and taken out from the iron tube.

The samples used for the measurements of electrochemical corrosion behaviors were polished with emery paper and buffed to a mirror finish. Each sample was sealed with epoxy resin except for an exposed surface of 10 mm×10 mm submitted to electrochemical tests in a three-electrode cell. The Pt sheet was used as the auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Potentiodynamic and galvanostatic experiments were performed with a CHI660D electrochemistry workstation in a 3.5% (mass fraction) NaCl solution. The anodic current density in the galvanostatic tests was 100 mA/cm² and the scan rate of potentiodynamic tests was 5 mV/s. The electrochemical impedance spectroscopy measurements were performed to study the kinetics of the electrode reactions with the CHI660D electrochemistry workstation and a Zview analyzer. The impedance measurements were made over a frequency range of 0.01–100 kHz with a 10 mV alternative current signal and interpreted in terms of equivalent circuit with frequency dependent components.

The microstructure and the morphology of corrosion surface of each sample were determined by SEM. The phase compositions and the corrosion products were determined by EDS and XRD.

3 Results and discussion

3.1 Effects of Hg and Ga on microstructures of Mg anode alloys

Figures 1(a), (b) and (c) show the scanning electron micrographs of the Mg–2%Hg, Mg–2%Ga and Mg–2%Hg–2%Ga alloys, respectively. It can be seen that there are white second-phases (arrow) at the grain boundaries of the two alloys. The size of the second-phases in the Mg–2%Hg–2%Ga alloy is larger than that in the Mg–2%Hg alloy. This demonstrates that the addition of Ga into the Mg–Hg alloy can increase the size of the second-phase. Combined with the EDS and XRD results (see Fig. 1(d) and Fig. 2), the white second-phases in the Mg–2%Hg–2%Ga alloy are Mg₃Hg and Mg₅Ga₂. The microstructure of the Mg–2%Ga alloy (Fig. 1(b)) shows homogeneous solid solution without second-phases precipitated.

3.2 Effects of Hg and Ga on electrochemical and corrosion behaviors of Mg anode alloys

To obtain information about the effects of Hg and Ga on the electrochemical activities of the Mg anode alloys, galvanostatic curves were tested on the Mg–2%Hg, Mg–2%Ga and Mg–2%Hg–2%Ga alloys in

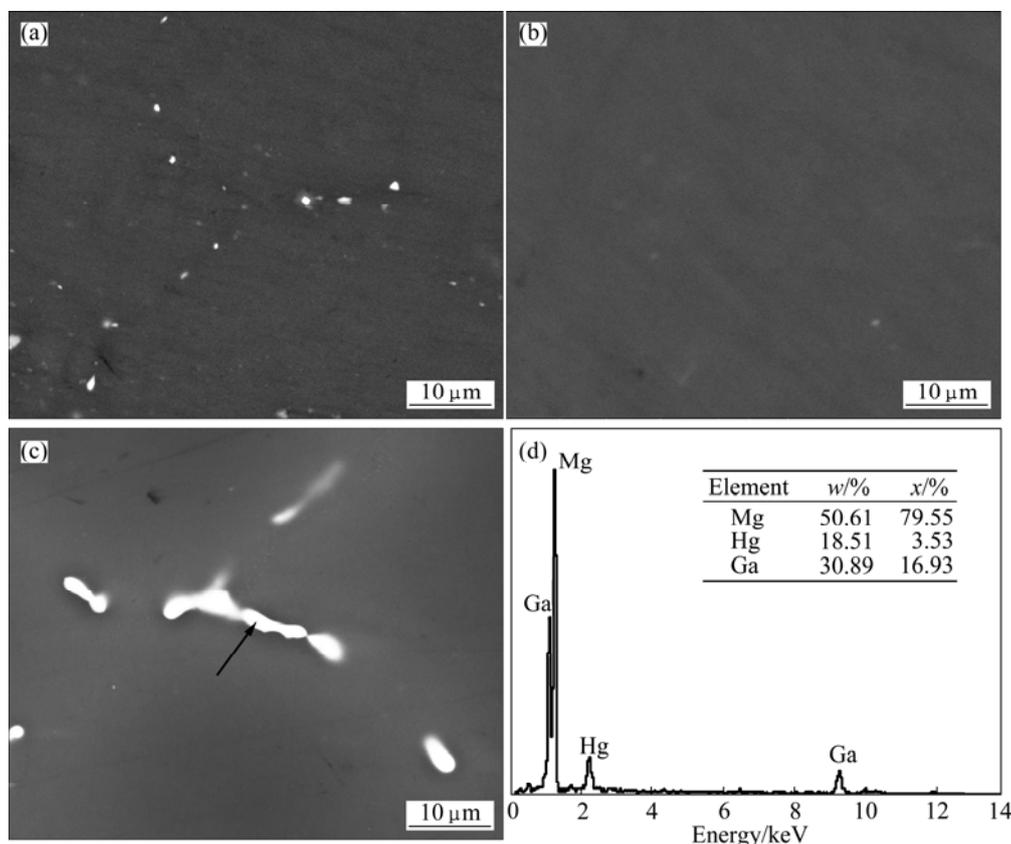


Fig. 1 SEM images (a, b, c) and emission spectrum (d) of Mg anode alloys: (a) SEM image of Mg–2%Hg; (b) SEM image of Mg–2%Ga; (c) SEM image of Mg–2%Hg–2%Ga; (d) EDS of Mg–2%Hg–2%Ga

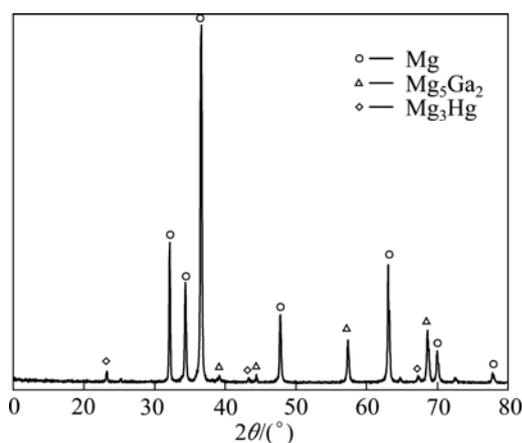


Fig. 2 X-ray pattern of Mg-2%Hg-2%Ga alloy

3.5% NaCl solution (Fig. 3). The anodic current density is 100 mA/cm².

As seen in Fig. 3, the Mg-2%Ga alloy shows obvious polarization behavior with the test time prolonging and the Mg-2%Hg alloy and Mg-2%Hg-2%Ga alloys show excellent electrochemical activities. Table 1 shows the mean potentials of the samples measured from the galvanostatic curves. The sample of the Mg-2%Hg-2%Ga alloy has the most negative mean potential of -1.848 V and the best electrochemical activity. The sequential negative potential occurs in the Mg-2%Hg alloy and the Mg-2%Ga alloy has the most positive mean potential of -1.48 V and the worst electrochemical activity. The addition of Ga in the Mg-Hg alloy anode can promote the electrochemical activity, but only adding Ga into the Mg anode does not show activation effect.

The electrochemical activity of the anode depends on the electrode surface state of the alloying elements during electrochemical reaction processing. Figure 4 shows the scanning electron micrographs and the energy dispersive spectroscopies of the corroded surfaces of the

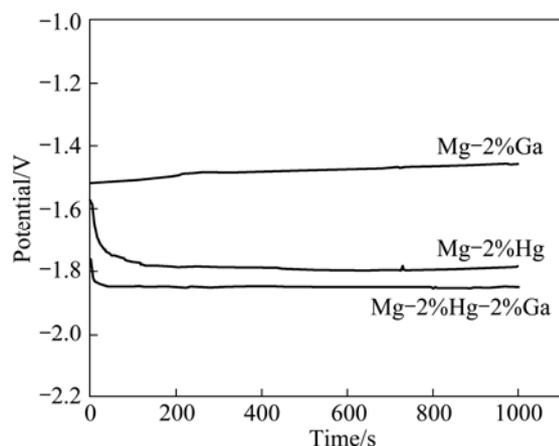


Fig. 3 Galvanostatic curves of Mg anode alloys at current density of 100 mA/cm²

Table 1 Electrochemical corrosion parameters of Mg anode alloys

Alloy	φ_{mean} (VS SCE)/V	φ_{corr} (VS SCE)/V	J_{corr} /(mA·cm ⁻²)
Mg-2%Hg	-1.78	-1.752	1.375
Mg-2%Ga	-1.48	-1.60	0.15
Mg-2%Hg-2%Ga	-1.848	-1.919	2.316

alloys after galvanostatic tests. It can be seen that spherical Hg ions deposit on the corrosion surface of the Mg-2%Hg alloy (Fig. 4(a)). Spherical Hg ions enter into a metallic contact with Mg atoms and form Mg amalgams, which react severely with moisture and form metal oxide film and pure liquid Hg. At the same time, the liquid Hg deposits on the electrode surface, strips the corrosion products of the surface and reacts with the α -Mg matrix, maintaining the activation dissolution process. Adding 2%Ga into the Mg-2%Hg alloy leads to the co-dissolution of Hg and Ga atoms. It can be demonstrated by the results of scanning electron micrographs of corroded surface and energy dispersive spectrometry of corrosion products of the Mg-2%Hg-2%Ga alloy (Fig. 4(c)). This accumulates liquid Ga because the exothermic Mg²⁺ hydrolysis reaction can enlarge the area of the Hg liquid and dissolve more Mg atoms. Moreover, the stripping effect of mutually soluble liquid Hg and Ga is larger than that of liquid Hg due to the smaller size of Ga atom than Hg atom. But when adding 2%Ga in the Mg anode, there is a small amount of Ga deposited on the corroded surface of the Mg-2%Ga alloy and the corrosion products accumulate on the electrode surface (Fig. 4(b)), so the activation effect is not obvious.

The electrochemical activity of the anode is also relevant on the microstructure morphology of the alloy. Figure 1 shows that there are second-phases in the Mg-2%Hg alloy and the Mg-2%Hg-2%Ga alloy. The second-phases have different electro-negativity from the α -Mg matrix, which acts as the cathode compared with the α -Mg matrix. The activation reaction of the surface begins from the interfacial zone between the α -Mg matrix and the second-phase. But the microstructure of the Mg-2%Ga alloy is solid solution and its surface has homogeneous electro-negativity, thus the activation dissolution of the matrix is slow. So the electrochemical activity of the Mg-2%Ga alloy is the worst.

Figure 5 shows the polarization curves of the Mg anode alloys in 3.5% NaCl solution. From the rest potential, the anode polarization shows remarkable increase in the anodic current density. Near the rest potential as the potential rises, the anodic dissolution rate increases linearly. The whole reaction is controlled by activation polarization.

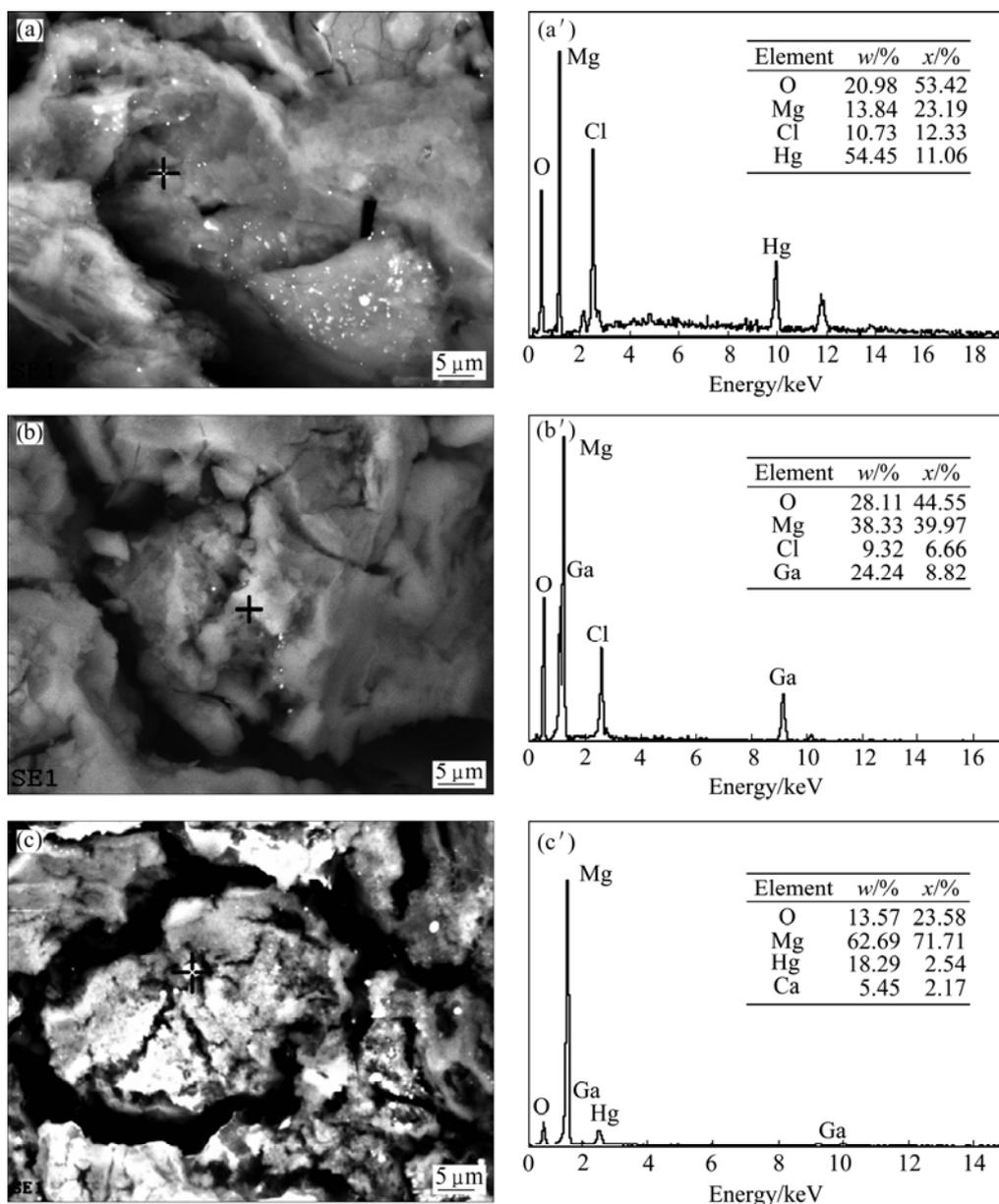


Fig. 4 SEM images of corroded surface (a, b, c) and energy dispersive spectrometry (a', b', c') of corrosion products of Mg anode alloys: (a), (a') Mg-2%Hg; (b), (b') Mg-2%Ga; (c), (c') Mg-2%Hg-2%Ga

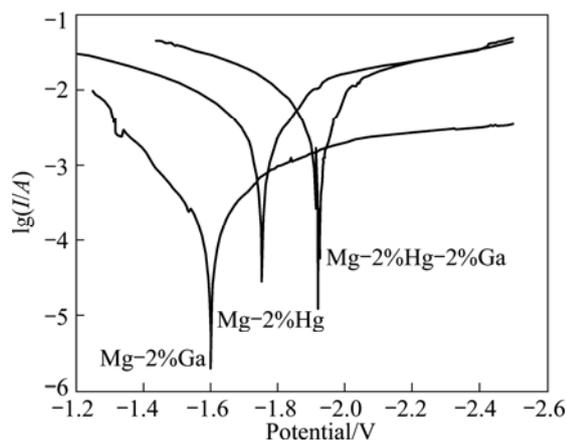


Fig. 5 Potentiodynamic curves of Mg anode alloys

It can be seen that the Mg-2%Ga alloy has more positive corrosion potential than the Mg-2%Hg or the Mg-2%Hg-2%Ga alloy. The corrosion current densities and corrosion potentials of the Mg anodes were calculated by Tafel linear extrapolation and listed in Table 1. The Mg-2%Ga alloy has the smallest corrosion current density and the best corrosion resistance, showing a corrosion current density of 0.15 mA/cm^2 . The Mg-2%Hg-2%Ga alloy has the largest corrosion current density and the worst corrosion resistance. The corrosion current density of the Mg-2%Hg-2%Ga alloy increases from 1.375 mA/cm^2 to 2.316 mA/cm^2 when 2%Ga is added.

The corrosion resistance of the Mg anode alloys is

relevant on the microstructure morphology and the chemical composition of the alloys. Figure 1 shows that there are second-phases at the grain boundaries of the Mg–2%Hg alloy and the Mg–2%Hg–2%Ga alloy. The second-phases have positive potential and act as the cathode compared with the α -Mg matrix. The two phases constitute of galvanic battery and decrease the corrosion resistance of the alloys. The Mg–2%Ga alloy has better corrosion resistance than the Mg–2%Hg alloy because the microstructure of the Mg–2%Ga alloy is solid solution, its surface has homogeneous electro-negativity, and the electro-negativity discrepancy between Mg and Ga is smaller than that between Mg and Hg. Moreover, Hg ions deposit on the electrode surface and form Mg amalgams, which have higher electro-negativity. The Mg–2%Hg–2%Ga alloy has the worst corrosion resistance because the amount of the alloy element is the most among the three alloys, and the galvanic corrosion driving force is the largest.

3.3 Electrochemical impedance spectroscopy (EIS) measurements

The electrochemical impedance spectroscopies for the Mg–2%Hg, Mg–2%Ga and Mg–2%Hg–2%Ga alloys at φ_{corr} in 3.5% NaCl solution are shown in Fig. 6. The Nyquist plots of the Mg–2%Hg alloy and Mg–2%Hg–2%Ga alloy are characterized by one capacitive loop at high frequency, while the Nyquist plot of the Mg–2%Ga alloy is characterized by two capacitive loops at high and low frequencies.

On the basis of the EIS results in Fig. 6, the equivalent circuits can be attained (see Fig. 7). In Fig. 7 R_s is the electrolyte resistance; C_1 is the capacitance of the double layer; R_1 is the charge transfer resistance in the faradaic reaction; C_2 and R_2 refer to the capacitance of the corrosion product film and the film resistance. A method of parameter fitting based on the equivalent circuits in Fig. 7 is applied and the results are listed in Table 2.

Compared with the values of the three Mg anode alloys in Table 2, the Mg–2%Hg–2%Ga alloy shows the lowest C_1 and R_1 values. The lowest C_1 and R_1 values lead to the lowest charge transfer resistance in the faradaic reaction and the smallest concentration polarization. The largest C_1 and R_1 values in the Mg–2%Ga alloy lead to the largest faradaic reaction impedance and largest concentration polarization. Based on the above results, the Mg–2%Hg–2%Ga alloy has the best electrochemical activity, and the Mg–2%Ga alloy has the worst electrochemical activity, which are consistent with the galvanostatic results. It is ascribed to the liquid Hg and Ga ions deposited on the corroded surface of the Mg–2%Hg–2%Ga alloy, and stripping the corrosion products of the anode surface. A capacitive

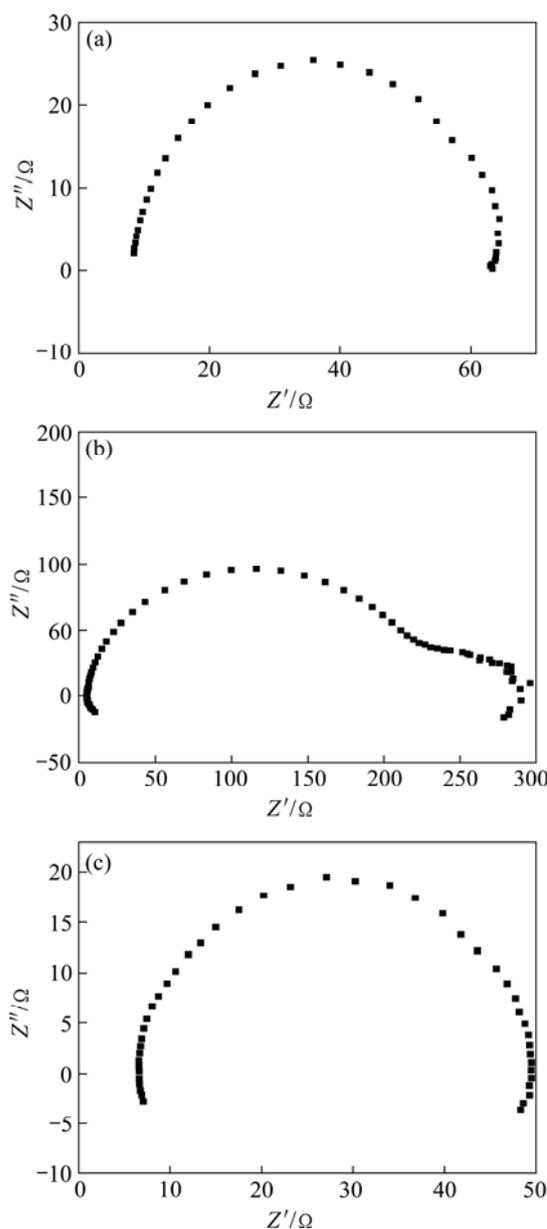


Fig. 6 Electrochemical impedance spectra of Mg anode alloys at φ_{corr} in 3.5% NaCl solution: (a) Mg–2%Hg; (b) Mg–2%Ga; (c) Mg–2%Hg–2%Ga

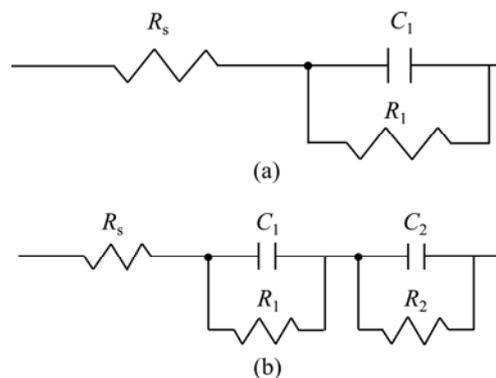


Fig. 7 Equivalent circuits of Mg anode alloys: (a) Mg–2%Hg and Mg–2%Hg–2%Ga; (b) Mg–2%Ga

Table 2 Electrochemical parameters obtained by fitting analysis of Nyquist diagrams of Mg anode alloys

Alloy	$R_s/(\Omega \cdot \text{cm}^2)$	$C_1/(\text{F} \cdot \text{cm}^{-2})$	$R_1/(\Omega \cdot \text{cm}^2)$	$C_2/(\text{F} \cdot \text{cm}^{-2})$	$R_2/(\Omega \cdot \text{cm}^2)$
Mg–2%Hg	7.696	1.166×10^{-5}	55.88		
Mg–2%Ga	6.113	1.383×10^{-5}	164.6	0.000386	80.17
Mg–2%Hg–2%Ga	6.731	1.107×10^{-5}	42.38		

loop occurs on the Nyquist plot of the Mg–2%Ga alloy at low frequency, which suggests that the corrosion products covers the anode surface, which impedes the diffusion of the reaction products. Therefore, the Mg–2%Ga alloy has the most positive mean potential as well as the smallest electrochemical activity.

4 Conclusions

1) The microstructure of the Mg–2%Ga alloy is solid solution and the Mg–2%Hg and Mg–2%Hg–2%Ga alloys have white second-phases at the grain boundaries. The results of EDS and XRD show that the white second-phases of the Mg–2%Hg–2%Ga alloy are Mg_3Hg and Mg_5Ga_2 .

2) The addition of 2%Ga in the Mg–2%Hg alloy decreases the mean potential from -1.78 V to -1.848 V, leading to better electrochemical activity, and increases the corrosion current density from 1.375 mA/cm^2 to 2.136 mA/cm^2 , reducing the corrosion resistance of the alloy.

3) The addition of Hg in the Mg anode forms Mg amalgams and strips the corrosion products. The addition of Ga in the Mg–Hg anode accelerates the stripping of the corrosion products, which decreases the faradaic impedance and promotes the electrochemical activity. Only adding Ga in Mg anode alloy does not strip the corrosion products, which impedes the diffusion of the reaction products. Therefore, the Mg–2%Ga alloy has the most positive mean potential as well as the smallest electrochemical activity.

References

- [1] ZHAO Hong-yang, BIAN Pei, JU Dong-ying. Electrochemical performance of magnesium alloy and its application on the sea water battery [J]. *Journal of Environmental Science*, 2009, 21(S1): 88–91.
- [2] RENUKA R. AgCl and Ag₂S as additives to CuI in Mg–CuI seawater activated batteries [J]. *Journal of Applied Electrochemistry*, 1997, 27(12): 1394–1397.
- [3] AURBACH D, SURESH G S, LEVI E, MITELMAN A, MIIRAH O, CHUSID O, BRUNELLI M. Progress in rechargeable magnesium battery technology [J]. *Advanced Materials*, 2007, 19: 4260–4267.
- [4] ALVAREZ-LOPEZ M, PEREDA M D, del VALLE J A, FERNANDEZ-LORENZO M, GARCIA-ALORISO M C, RUANO O A, ESCUDERO M L. Corrosion behavior of AZ31 magnesium alloy with different grain sizes in simulated biological fluids [J]. *Acta Biomaterialia*, 2010, 6: 1763–1771.
- [5] WU Chang-sheng, ZHANG Zhao, CAO Fa-he, ZHANG Li-jun, ZHANG Jian-qing, CAO Chu-nan. Study on the anodizing of AZ31 magnesium alloys in alkaline borate solutions [J]. *Surface Science*, 2007, 253: 3893–3898.
- [6] DENG Shu-hao, YI Dan-qing, ZHAO Li-hong, WANG Bin, JI Cheng-nian, LAN Bo. Study on Mg alloy anode material for seawater battery [J]. *Power Source*, 2007, 31(5): 402–405.
- [7] FENG Yan, WANG Ri-chu, YU Kun, PENG Chao-qun, ZHANG Jia-pei, ZHANG Chun. Activation of Mg–Hg anodes by Ga in NaCl solution [J]. *Journal of Alloys and Compounds*, 2008, 54(5): 1–5.
- [8] AUNG N N, ZHOU Wei. Effect of grain size and twins on corrosion behavior of AZ31B magnesium alloy [J]. *Corrosion Science*, 2010, 52: 589–594.
- [9] WANG Nai-guang, WANG Ri-chu, YU Kun, FENG Yan, PENG Chao-qun. Effect of alloying and heat treatment on electrochemical behavior of Mg anode [J]. *The Chinese Journal of Nonferrous Metals*, 2009, 19(1): 40–43. (in Chinese)
- [10] LI Guan-qun, WU Guo-hua, FAN Yu, DING Wen-jiang. Effect of the main alloying element on microstructure and corrosion resistance of magnesium alloys [J]. *Foundry Technology*, 2006, 27(1): 79–82.
- [11] HOU Jun-cai. Study on preparation and performance of high-potential magnesium sacrificial anodes [D]. Zhengzhou: Zhengzhou University, 2006. (in Chinese)
- [12] HOU Jun-cai, GUAN Shao-kang, REN Chen-xing, XU He, FANG Zhong-xue, ZHAO Yan-xue. Effect of small addition of strontium on microstructure and electrochemical performance of Mg–Mn sacrificial anode [J]. *Journal of Chinese Society for Corrosion and Protection*, 2006, 26(3): 166–170.
- [13] BRESLIN C B, CARROLL W M. Electrochemical behavior of aluminum activated by gallium in aqueous electrolytes [J]. *Corrosion Science*, 1992, 33: 1735–1746.
- [14] BESSONE J B. The activation of aluminum by mercury ions in non-aggressive media [J]. *Corrosion Science*, 2006, 48: 4243–4256.
- [15] FLAMINI D O, SAIDMAN S B, BESSONE J B. Aluminum activation produced by gallium [J]. *Corrosion Science*, 2006, 48: 1413–1425.
- [16] YU Zu-xiao, HAO Shi-xiong, GONG Min. Effect of trace HgCl_2 on the electrochemical behavior of aluminum anode [J]. *Battery Bimonthly*, 2005, 35(5): 368–370.

Hg 和 Ga 元素对 Mg 阳极材料组织和电化学腐蚀性能的影响

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摘 要: 采用动电位极化、恒电流和交流阻抗测试方法研究了 Hg 和 Ga 元素对 Mg-2%Hg, Mg-2%Ga 和 Mg-2%Hg-2%Ga 合金电化学腐蚀性能的影响, 并用扫描电镜、X 射线衍射和能谱分析了上述合金的显微组织和腐蚀表面形貌。结果表明: Mg-2%Ga 合金是固溶体, Mg-2%Hg 和 Mg-2%Hg-2%Ga 合金的晶界有白色第二相。Mg-2%Ga 合金的平均电位为 -1.48 V, 腐蚀电流密度为 0.15 mA/cm², 电化学活性差, 耐腐蚀性能好。Mg-2%Hg-2%Ga 合金的平均电位 -1.848 V, 腐蚀电流密度为 2.136 mA/cm², 电化学活性好, 耐腐蚀性能差。Mg-Hg-Ga 合金的活化机制是 Hg 和 Ga 原子的溶解-沉积。

关键词: Mg 阳极合金; 显微组织; 电化学活性; 耐腐蚀性能; 交流阻抗图谱

(Edited by YANG Hua)