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Influence of Ga and In on microstructure and electrochemical properties of Mg anodes

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Abstract: The influence of Ga and In on the electrochemical properties of Mg anode materials were investigated by the polarization and galvanostatic curve tests. The microstructure and the corroded surface of the Mg−In−Ga alloys were observed by scanning electron microscopy (SEM). The corrosion product of the Mg−0.8%In (mass fraction) and Mg−0.8%Ga−0.3%In alloy were determined by X-ray diffraction. The results show that no second phase exists in the Mg−*x*In (*x*=0−0.8%) allloys. Intergranular compounds containing Ga and In elements occur in the Mg−0.8%In−*x*Ga (*x*=0−0.8%) alloys. The addition of In into Mg as well as the addition of 0.05%−0.5%Ga into Mg−In alloy promotes the corrosion resistance. The addition of Ga into Mg−In alloys also promotes the electrochemical activity. The Mg−0.8%In−0.8%Ga alloy has the most negative mean potential, −1.682 V, which is more negative than −1.406 V in AZ91D. The corrosion type of the Mg−In−Ga alloys is general corrosion and the corrosion product is $Mg(OH)_2$.

Key words: Mg anode; alloying element; Ga; In; galvanostatic curve; corrosion resistance; electrochemical activity

1 Introduction

Mg alloys are widely used in high energy density batteries and sacrificial anodes due to many advantages, such as rapid activation, low specific mass, low electrode potential and high current capacity [1−5]. Since 1960 s, Mg alloy batteries have been the subject of comprehensive interest and have been developed for some military and commercial applications, such as torpedo, electromotive and unmanned underwater vehicle power source.

The developed Mg anode materials with high cell voltage are AP65 (Mg−6%Al−5%Pb) [6,7], Mg−7%Tl−5%Al [1] and Mg−Hg−Ga alloys [8]. The specific energy of the seawater battery using Mg−Hg−Ga alloys as anode can reach 150 W·h/kg [9,10], compared with 30 W·h/kg of lead acid battery. The open potential of Mg−Hg alloys in a 3.5% NaCl solution is −2.0 V (vs SCE) [8], compared with −1.8 V (vs SCE) of Mg−6%Al−5%Pb alloys [6]. However, the good results of the Mg anodes obtained in high power seawater battery still meet with problems such as bad deformability, large self-corrosion velocity and low current efficiency [9,10]. Especially the Cl^- in seawater produces acid environment for the Mg anodes and increases corrosion of the Mg anodes [11−14]. In order to solve these problems, some alloying elements with high over-potential of hydrogen revolution and large electrochemical activity, such as In, Zn, Mg and Re elements, were added into Mg anodes in recent years [15−18].

According to Refs. [8,13,19−24], Ga and Hg can greatly activate Mg anodes due to the dissolution-redeposition mechanism and Ga can also enhance the corrosion resistance of the amalgams [25]. Due to the toxicity of Hg, In is chosen to replace Hg. In this work, the effect of Ga and In on electrochemical corrosion behavior of Mg anode materials was studied.

2 Experimental

The Mg−In and Mg−In−Ga alloys, with the given chemical compositions shown in Table 1, were sealed in Fe flask under Ar atmosphere and melted in muffle. The chemical composition of the specimens was determined by emission spectrum analysis (ESA) and atomic

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Table 1 Chemical compositions of Mg−In−Ga alloys

Sample	*x*/%				
	In	Ga	Fe	Ca	Mg
Mg−0.05%In	0.048	0	0.088	0.030	Bal.
Mg−0.1% In	0.102	0	0.075	0.042	Bal.
Mg−0.3% In	0.294	0	0.061	0.045	Bal.
Mg−0.5% In	0.505	0	0.077	0.040	Bal.
Mg−0.8% In	0.812	0	0.084	0.035	Bal.
Mg−0.8%In−0.05%Ga	0.801	0.053	0.090	0.030	Bal.
Mg−0.8%In−0.1%Ga	0.805	0.111	0.086	0.038	Bal.
Mg−0.8%In−0.3%Ga	0.798	0.313	0.078	0.041	Bal.
Mg−0.8%In−0.5%Ga	0.810	0.495	0.082	0.048	Bal.
Mg−0.8%In−0.8%Ga	0.802	0.810	0.065	0.032	Bal.

absorption spectrochemical analysis. The small amounts of impurities such as Fe and Ca were confirmed. The alloys were prepared three times and the deviation of the main composition is under 0.5%.

Microstructure and corroded surface of the specimens were observed using SEM (KYKY−2800). The corrosion product was determined by XRD with a Rigaku D/Max 2500 V diffractometer with Cu K_α radiation.

Potentiodynamic and galvanostatic experiments were performed with a Potentiostat-Galvanostat (Model 263A) in a 3.5% NaCl solution. The scanning rate of potentiodynamic measurement is 5 mV/s and the anodic current density in the galvanostatic test is 180 mA/cm^2. The specimens were polished with emery paper and buffed to a mirror finish. Each of them was sealed with epoxy resin except for an exposed surface of 10 mm×10 mm submitted to the electrochemical tests in a three-electrode cell. A platinum sheet was used as the auxiliary electrode and a SCE with a standard electrode potential of 0.2412 V(SHE) was used as the reference electrode.

3 Results and discussion

3.1 Effect of Ga and In on microstructure

Figure 1 shows the SEM images of the cast Mg−In and Mg−In−Ga alloys. From Figs. 1(a) and (b), it can be seen that no second phase exists in the Mg−In specimens. Figures 1(c) and (d) show that intergranular compounds containing Ga and In elements exist in the Mg−In−Ga alloys. The amount of the intergranular compounds increases and the grain size decreases when the Ga content increases from 0.3% to 0.8%. According to ESA measurements in Fig. 2, the intergranular compound in Mg−0.8%In−0.3%Ga alloy contains 2.09% In, 1.51% Ga and the intergranular compound in Mg−0.8%In−0.8%Ga alloy contains 2.52% In, 2.32% Ga. The addition of Ga in Mg−In alloys inspires the formation of the intergranular compounds containing Ga and In.

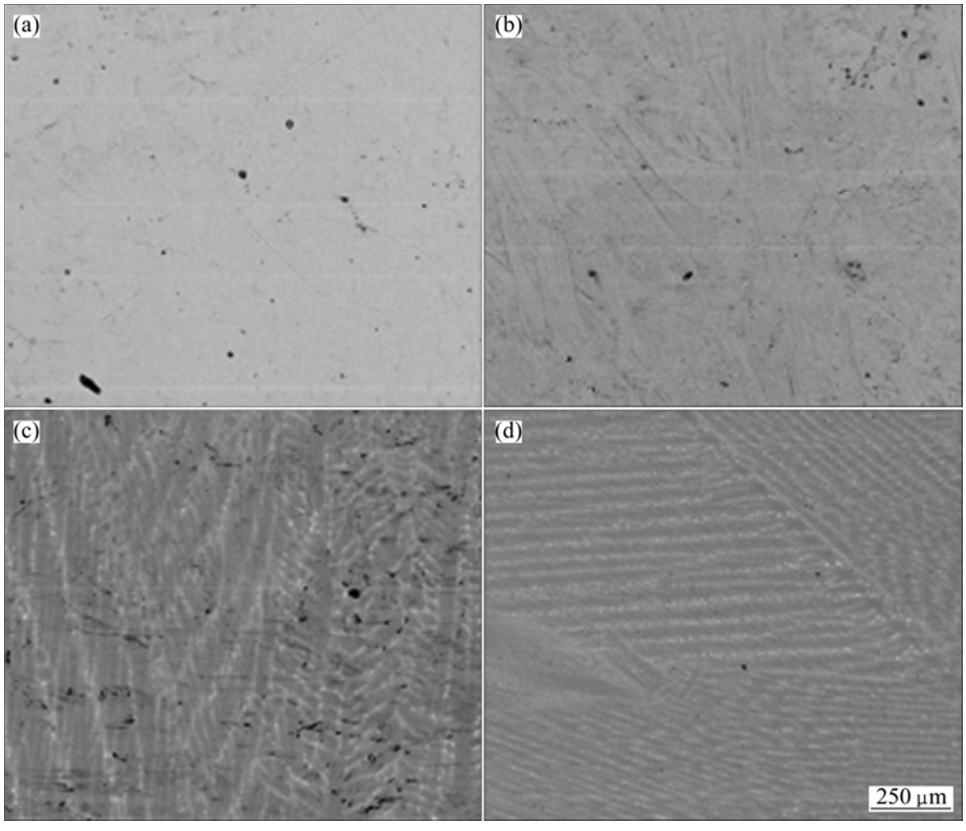

Fig. 1 SEM images of Mg−Ga−In alloys: (a) Mg−0.3% In; (b) Mg−0.8%In; (c) Mg−0.8%In−0.3%Ga; (d) Mg−0.8%In−0.8%Ga