

Influence of freezing rate on microstructure and electrochemical properties of Mg-2%Ga alloys

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Abstract: Equilibrium freezing curve of Mg-2%Ga (mass fraction) alloy was calculated by CALPHAD method. Microstructures of the melted Mg-2%Ga alloys solidified by iron and copper moulds, respectively, were investigated using OM and SEM. Electrochemical properties of the Mg-2%Ga alloys with different freezing rates were measured by galvanostatic, potentiodynamic and electrochemical impedance spectroscopy tests. The results show that solidification by copper mould leads to intergranular Mg_3Ga_2 compounds with small size and large number density. Less adsorbent of Mg^+ and oxide corrosion products occur on the surface of the Mg-2%Ga alloys solidified by copper mould, producing lower corrosion current density of $1.8 \times 10^{-5} \text{ mA/cm}^2$. In the galvanostatic tests with 100 mA/cm^2 current density, more negative stable potential of -1.604 V exists in the Mg-2%Ga alloys solidified by iron mould due to the lower freezing rate, which leads to smaller inductive and capacity time constants as well as shorter activity time and better electrochemical activity.

Key words: Mg-Ga alloy; electrode materials; electrochemical reaction; microstructure; computer simulation

1 Introduction

Magnesium alloys are widely used in seawater batteries and sacrificial anodes due to many advantages, such as rapid activation, low specific mass, low electrode potential and high current capacity[1–3]. Since 1960s, magnesium 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 magnesium anode materials with high cell voltage are AP65 (Mg-6%Al-5%Pb), Mg-7%Ti-5%Al[1] and Mg-Hg alloys[4]. The seawater battery using Mg-Hg alloys as anodes can reach a higher specific energy of $150 \text{ W} \cdot \text{h/kg}$ [5–6], compared with lead acid battery of $30 \text{ W} \cdot \text{h/kg}$. 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[7–8]. In order to solve these problems, gallium was added into magnesium anodes due to its high hydrogen evolution over-potential and good electrochemical activity[4, 9–11]. For getting fine microstructure, heat treatment of

the Mg-Ga anode materials was studied[12–14]. But there are few reports about the influence of the solidifying rates on the electrochemical and corrosion properties of the Mg-Ga alloys. According to researches in Ref.[15], fine distribution of the alloying elements in magnesium anode materials does not imply good anodic properties. The present study will focus on the influence of the solidifying rate on the microstructure and electrochemical properties of the Mg-2%Ga alloys.

2 Experimental

The Mg-2%Ga (mass fraction) alloys were melted in a muffle furnace using 99.9% purity materials and then solidified by iron and copper mould, respectively. The chemical compositions of the specimens were determined by atomic absorption spectrochemical analysis. The deviation of the main composition was under 0.5%.

Microstructure and corroded surface of the specimens were observed using OM and SEM. And SEM observation was carried out using Sirion 200. Potentiodynamic and galvanostatic experiments were performed with a Potentiostat-Galvanostat (Model 263A) in 3.5% (mass fraction) NaCl solution. The scanning rate

of potentiodynamic test was 5 mV/s and the anodic current density in the galvanostatic test was 100 mA/cm² and the testing time was 1 300 s. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Potentiostat-Galvanostat (Model 263A) and a 1255 Solartron frequency response analyzer. The impedance measurements were made over a frequency range of 0.005 Hz to 100 kHz (15 points per decade) with a 10 mV AC signal and interpreted in terms of equivalent circuit (EC) with frequency dependent components. Those 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 saturated calomel electrode (SCE) was used as the reference electrode.

3 Results and discussion

3.1 Calculation of equilibrium freezing curve of Mg-2%Ga alloy

Using CALPHAD method and the Mg-Ga thermodynamic database[16], the equilibrium freezing curve of the Mg-2%Ga liquid alloys was calculated (Fig.1). Mg with HCP structure was first solidified in Mg-2%Ga liquid alloys. The number of the HCP phase increased with decreasing the temperature. When the temperature decreased to nearly 415 °C, Mg₅Ga₂ was solidified from the liquid and the temperature did not change until total solidification of liquid. Finally, the Mg-2%Ga alloy contained about 2.8% Mg₅Ga₂ and 97.2% Mg.

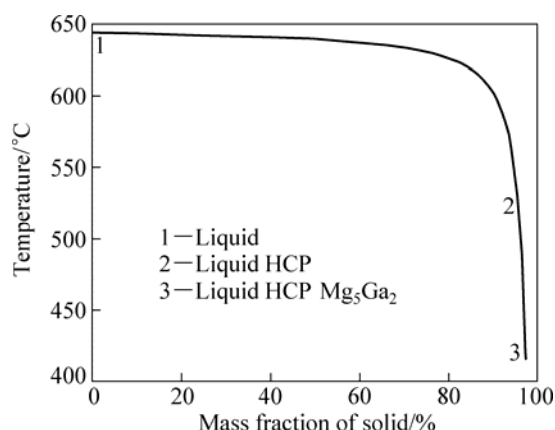


Fig.1 Equilibrium freezing curve of Mg-Ga alloy

Figure 2 shows the composition of the Mg-2%Ga liquid alloy during equilibrium freezing. It can be seen that the content of Mg in the Mg-2%Ga liquid alloy decreases with decreasing the temperature, while the content of Ga increases. This leads to the solidification

of Mg₅Ga₂ compounds at the last stage.

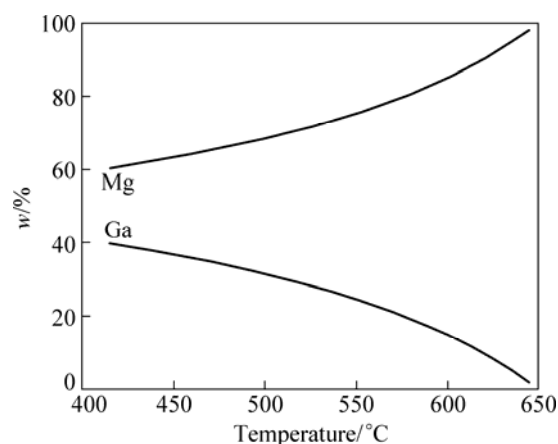


Fig.2 Composition of Mg-Ga liquid alloy during equilibrium freezing

3.2 Influence of freezing rate on microstructure of Mg-2%Ga alloy

Figure 3 shows the microscopic structures of the Mg-2%Ga alloy with different freezing rates. According to the calculated freezing curve, the intergranular and transgranular compounds are Mg₅Ga₂ in the Mg-2%Ga alloys. From Fig.3 it can be observed that the Mg-2%Ga alloy solidified by copper mould has smaller grain size and larger number density of Mg₅Ga₂ compounds than the alloy solidified by iron mould. It may be due to the fast freezing rate.

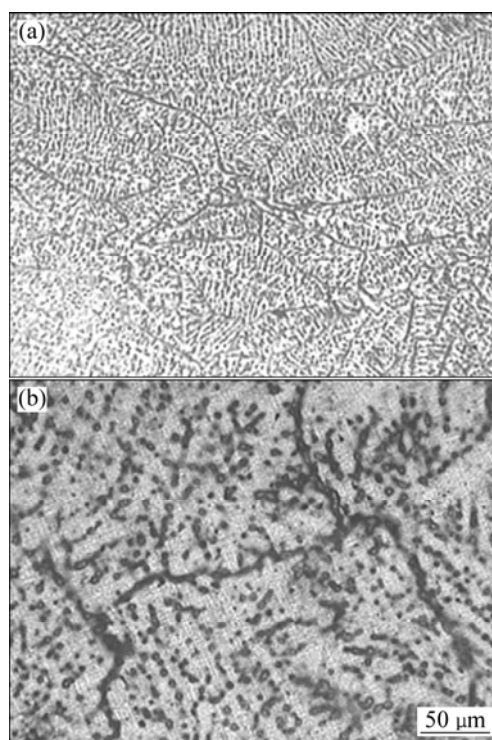


Fig.3 Microscopic structures of Mg-2%Ga alloys with different freezing rates solidified by copper mould (a) and iron mould (b)

3.3 Influence of freezing rate on electrochemical corrosion behavior

3.3.1 DC measurements

To obtain information about the influence of freezing rate on the electrochemical corrosion behavior of the Mg-2%Ga alloys, galvanostatic and potentiodynamic curves were conducted in a 3.5 mol/L NaCl solution (Fig.4). The activation of the surface is confirmed by the trend of the curve $\varphi-t$. The stable potential was calculated from the curves (Table 1). From Fig.4(a) and Table 1, it can be observed that polarization exists in the Mg-2%Ga alloy solidified by copper mould but stable potential of -1.604 V was obtained in the alloy solidified by iron mould, which demonstrates better electrochemical activity.

During potentiostatic polarizations, a steady state current was attained for each applied potential step. Near

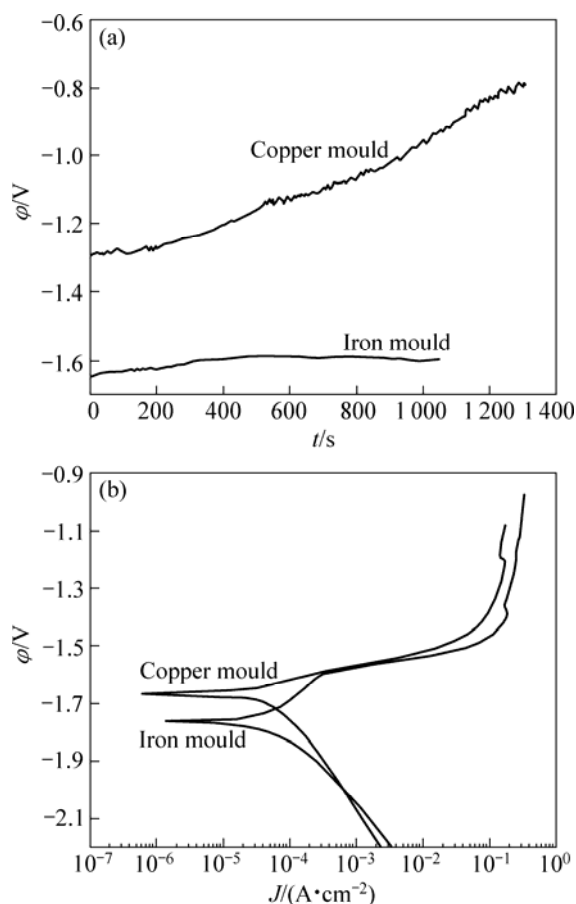


Fig.4 Galvanostatic and potentiodynamic curves of Mg-2%Ga alloys: (a) Galvanostatic curves; (b) Potentiodynamic curves

Table 1 Electrochemical corrosion properties of Mg-2%Ga alloys

Mould	φ_{stable}/V	$J_{corr}/(10^{-8} A \cdot cm^{-2})$	φ_{corr}/V	φ_{pit}/V
Iron	-1.604	6.3	-1.763	-1.60
Copper	Polarization	1.8	-1.665	-1.59

the rest potential the anodic dissolution rate increases with the increase of the potential, and steeper anodic polarization curves exist in the alloy solidified by iron mould. Pitting potential of about -1.60 V occurs in the Mg-2%Ga alloys with different freezing rates. From the galvanostatic measurements, it can be seen that the stable potential of the alloy solidified by iron mould is close to -1.6 V. The oxide film in this alloy destroyed quickly in the measurement, which leads to dissolution of the Mg matrix. The stable potential of the alloy solidified by copper mould is close to -1.3 V, which is more positive than pitting potential. So the oxide film on the surface is hard to destroy, which impedes the electrochemical activation reaction and leads to polarization in the galvanostatic measurements.

The corrosion potentials and corrosion current densities, calculated by Tafel linear extrapolation, are listed in Table 1. It can be seen that the corrosion current density of the alloy solidified by iron mould is 3.5 times the one of the alloy solidified by copper mould. It may be due to the damage of the oxide film on the surface. Figure 5 shows the corrosion surface of the alloys after potentiodynamic measurements. It can be observed that a lot of loose corrosion products exist in the alloy solidified by iron mould while compact oxide film exists in the alloy solidified by copper mould. The corrosion resistance depends on the properties of two electric poles in galvanic couple corrosion. According to the microscopic structures of the alloys in Fig.3(a), the closer grain and larger number density of second phases in the alloy solidified by copper mould lead to more

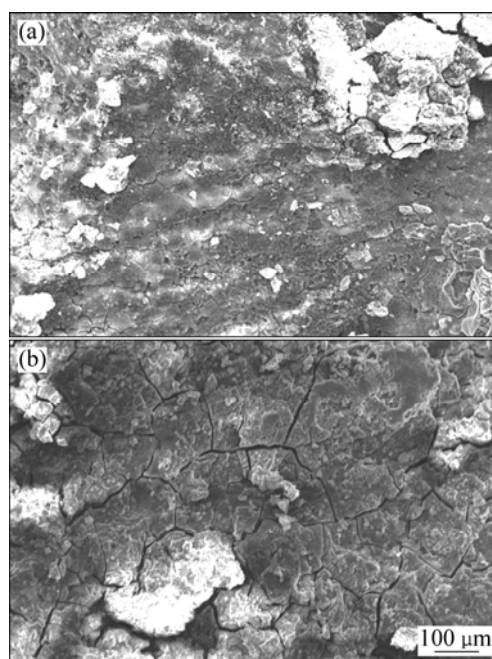


Fig.5 Corrosion surface of Mg-2%Ga alloys after potentiodynamic measurements: (a) Solidified by copper mould; (b) Solidified by iron mould

homogeneous structure and smaller corrosion driving force.

3.3.2 AC measurements

The EIS results are shown in Fig.6. It can be observed that capacitive impedance appears in high frequency. Inductive reactance appears in low frequency and two time constants occurs in the bode diagrams. The EC can be attained, as shown in Fig.7, where R_0 is the electrolyte resistance; C_{dl} and R_{ct} refer to the capacitance of the double layer and the charge transfer resistance in the Faradic reaction; L and R_u refer to the inductive

reactance and resistance of adsorbent of Mg^{+} and oxide on the surface. A method of parameter adjustment based on the equivalent circuit in Fig.6 was applied and the results are shown in Table 2.

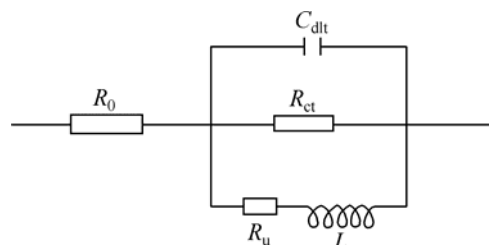


Fig.7 Equivalent circuits of Mg-2%Ga alloys/3.5% NaCl interfaces

Table 2 Electrochemical parameters obtained by fitting analysis of Nyquist diagrams of Mg-2%Ga alloys

Mould	$R_0/$ ($\Omega \cdot \text{cm}^2$)	$C_{dl}/$ ($\mu\text{F} \cdot \text{cm}^{-2}$)	$R_{ct}/$ ($\Omega \cdot \text{cm}^2$)	$L/$ ($\text{H} \cdot \text{cm}^2$)	$R_u/$ ($\Omega \cdot \text{cm}^2$)
Iron	2.804	9.291	370.7	4 303	660
Copper	1.251	7.989	508.3	7 477	1 047

The equation of $\tau = L/R_u$ is the time constant of the inductive reactance, which presents the stable time of the inductive reactance. The expression of $R_{ct}C_{dl}$ presents the stable time of the electric double layer. From Table 2, the values of τ in the Mg-2%Ga alloys solidified by iron and copper mould can be calculated to be 6.52 and 7.14, respectively. The values of $R_{ct}C_{dl}$ in the Mg-2%Ga alloys solidified by iron and copper moulds can be calculated to be 3 444.2 and 4 060.8, respectively. According to Ref.[17], smaller time constants of the capacitive impedance and inductive reactance lead to shorter activity time and better electrochemical activity. So the Mg-2%Ga alloy solidified by iron mould has more negative stable potential than the Mg-2%Ga alloy solidified by copper mould, as seen in Fig.4(a).

Considering that R_u refers to the resistance of adsorbent of Mg^{+} and oxide on the surface, it can be seen that smaller value of R_u in the Mg-2%Ga alloy solidified by copper mould leads to smaller number density of the adsorbent. It produces smaller moving resistance of the reactant H^{+} , resultant $Mg(OH)_2$ and reaction promoter Cl^{-} in the corrosion reaction. Reversely, the larger value of R_u in the Mg-2%Ga alloy solidified by iron mould leads to larger number density of the adsorbent of Mg^{+} and oxide on the surface. This increases moving resistance of the reactant H^{+} , resultant $Mg(OH)_2$ and reaction promoter Cl^{-} in the corrosion reaction and decreases the velocity of the corrosion reaction. The Mg-2%Ga alloy solidified by iron mould has larger corrosion current density than the alloy solidified by copper mould, as seen in Table 1.

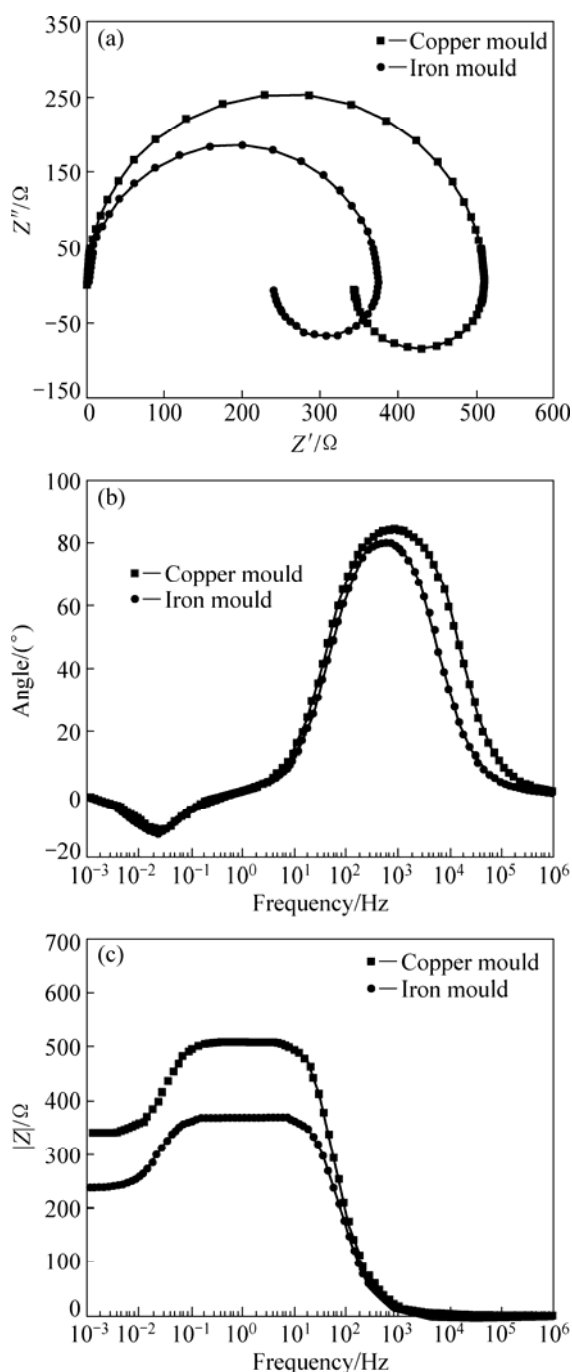


Fig.6 Nyquist and Bode diagrams of Mg-2%Ga alloys in 3.5%NaCl solution

4 Conclusions

1) Using CALPHAD method the equilibrium freezing curve of the Mg-Ga liquid alloys was calculated. Through thermodynamic calculation the Mg-2%Ga alloy after equilibrium freezing contains 2.8% Mg_5Ga_2 and 97.2% Mg.

2) High freezing rate exists in the Mg-2%Ga alloys solidified by copper mould and leads to smaller size of grain and larger number density of intergranular Mg_5Ga_2 compounds. Due to less adsorbent of Mg^+ and oxide corrosion products on the surface, lower corrosion current density of $1.8 \times 10^{-5} \text{ mA/cm}^2$ occurs in the Mg-2%Ga alloy solidified by copper mould.

3) In the galvanostatic measurements with current density of 100 mA/cm^2 , more negative stable potential of -1.604 V occurs in the Mg-2%Ga alloy solidified by iron mould due to the lower freezing rate. This is due to small inductive and capacity time constants as well as short activity time and better electrochemical activity.

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凝固速度对 Mg-2%Ga 合金显微组织和电化学性能的影响

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摘 要: 采用 CALPHAD 方法计算 Mg-2%Ga 合金的平衡凝固曲线。分别采用铁模和铜模冷却, 用熔炼铸造法制备该合金, 并用金相 OM 和扫描电镜 SEM 方法分析其显微组织, 用恒电流法、动电位扫描和交流阻抗法测量不同冷却速对 Mg-2%Ga 合金电化学性能的影响。结果表明: 铜模冷却的 Mg-2%Ga 合金晶界存在尺寸小、数量多的 Mg_5Ga_2 化合物, 其合金表面吸附了较少的 Mg^+ 和氧化腐蚀产物, 因此产生较低的腐蚀电流密度 $1.8 \times 10^{-5} \text{ mA/cm}^2$ 。铁模冷却的 Mg-2%Ga 合金在恒流 100 mA/cm^2 检测时具有更负的稳定电位 -1.604 V , 这是由于铁模冷却产生较低冷却速度导致双电层具有较小的感抗和容抗时间常数, 因此产生较短的活化时间和更好的电化学活性。

关键词: Mg-Ga 合金; 电极材料; 电化学反应; 显微组织; 计算机模拟

(Edited by YANG Hua)