Influence of Ga/Hg Ratio on Phase Constituents and Electrochemical Performance of Mg-Hg-Ga Anode Materials

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Abstract. This study investigated the impacts of Mg-Hg-Ga alloys of various Ga/Hg ratios on phase constituents and electrochemical performance. The relationship between composition and phase constituents of the casting alloys were investigated by SEM and XRD. Potentiodynamic polarization curves and the galvanostatic curves of the alloys in 3.5wt% NaCl solution were obtained. With a Ga/Hg ratio greater than 0.97, the second phase changes from Mg3Hg to Mg5Ga2, and the normal eutectic becomes a divorced eutectic. Additionally, corrosion is inhibited and passivation appears with an increase in the Ga/Hg ratio increase. With a starting Ga/Hg ratio of less than 0.68, the discharge process becomes steadier and discharge time simultaneously increases with the Ga/Hg ratio. Mg-Hg-Ga alloys with a 0.68 Ga/Hg ratio are suitable as the anode material for seawater batteries.

1. Introduction
Magnesium alloys are used widely as anode sheets for seawater batteries due to their high specific energy, long-term storage, stable discharge performance and fast activation [1-3]. For example, magnesium alloy seawater batteries are extensively used in torpedoes and some kinds of life jackets [4]. Mg-Hg alloys of 1~3wt% Hg are typically regarded as the best known seawater battery anode materials. The specific energy of a seawater battery can reach 150Wh/kg. The addition of an suitable amount of Hg may inhibit microgalvanic corrosion, and thus reduce the thickness of corrosion film on alloy surfaces; Mg3Hg as the second phase may also activate a magnesium matrix [5,6]. However, these properties are often accompanied by disadvantages such as significant self-corrosion and short discharge times [7,8].

Previous research has attempted to addition of Ga to the Mg anode material, resulting in improved electrochemical performance of the anode material due to the activation effect of Ga on the Al anode [9,10]. However, the influence of Ga on the alloy solidification structure and the discharge process remains unclear. This study prepared Mg-Hg-Ga alloys of various Ga/Hg ratios to analyze the effect of the ratio on the microstructure and electrochemical performance of Mg-Hg-Ga anode materials, such as those utilized in seawater batteries.

2. Experimental Method
Hg and Ga are volatile elements at high temperatures, requiring the pre-preparation of Mg–Hg and Mg-Ga master alloys; other alloys were obtained by dilution. Pure magnesium (99.99%) was melted in
a resistance furnace under the protection of gaseous CO$_2$ and SF$_6$. The pre-prepared Mg-Hg and Mg-Ga master alloys were then added into the melt at 600°C. The melt was stirred vigorously, and then cast into a water-cooled metallic mold. Table 1 lists the chemical compositions of tested alloys, which determined by ICP-AES.

Table 1. Chemical compositions and Ga/Hg ratios of alloys (wt%).

| Samples | Hg  | Ga  | Mg  | Ga/Hg |
|---------|-----|-----|-----|-------|
| MHG1    | 1.77| 0.83| Balance | 0.47 |
| MHG2    | 1.70| 1.16| Balance | 0.68 |
| MHG3    | 1.72| 1.67| Balance | 0.97 |
| MHG4    | 1.74| 1.95| Balance | 1.12 |

The microscopic structures of the magnesium alloys were observed by SEM (JEOL JSM-6301F) equipped with EDS. Electrochemical experiments were conducted with a potentiostat/galvanostat model 273A in 3.5wt% NaCl solution. The counter electrode consisted of a platinum plate, and the reference electrode consisted of a SCE. All potentials were referred to the SCE. The potentiodynamic test employed a scanning rate of 5mV/s. The current density of the galvanostatic measurements was 100mA/cm$^2$. All samples were ground to 1200 grit, and then polished using 1µm diamond polishing paste.

3. Results and discussion

The alloy microstructures are displayed in Figure 1. All alloys consist primarily of an $\alpha$-Mg matrix with eutectic phase distributed in the grain boundaries. All alloys also display well-developed $\alpha$-Mg dendrites and sixfold symmetry due to their rapid solidification when cast in the water-cooled metallic mold, as shown in Figure 1(c).

The X-ray Diffraction (XRD) spectral lines of four prepared alloys are displayed in Figure 2. Alloys MG1 and MG2 displayed the Mg$_3$Hg phase, while the Mg$_5$Ga$_2$ phase was found in alloys MG3 and MG4. These results indicate that the secondary phase of Mg-Hg-Ga alloys changes from Mg$_3$Hg to Mg$_5$Ga$_2$ with an increase in the Ga/Hg ration. As shown in Figures 1(a) and (b), when the Ga/Hg
ratio is less than 0.68, the microstructures of Mg-Hg-Ga alloys are composed primarily of eutectic \( \alpha \)-Mg and \( \alpha \)-Mg+Mg\(_3\)Hg, which is similar to the structure of the Mg-Hg alloy without Ga.[11,12]. However, when the Ga/Hg ratio is increased to 0.97, the Mg\(_5\)Ga\(_2\) phase appeared in alloys MHG3 and MHG4, and the Mg\(_3\)Hg phase was absent. Thus, experimental results indicate that Mg\(_5\)Ga\(_2\) inhibits the phase formation of Mg\(_3\)Hg.

![Figure 2. XRD spectral lines of Mg\(_3\)Hg and Mg\(_5\)Ga\(_2\) alloys](image)

![Figure 3. Potentiodynamic polarization curves of alloys in 3.5 wt% NaCl.](image)

Figure 3 depicts the potentiodynamic polarization curves of alloys in 3.5 wt% NaCl. Table 2 lists the experimental curves as fitted by the Tafel method with CorrView software. When the ratio of Ga/Hg was increased from 0.47 to 0.97, the corrosion current density \( (i_{corr}) \) decreased from 5.23 to 1.95; when the Ga/Hg ratio reached 1.12, the corrosion current density rapidly decreased to 0.025 mA/cm\(^2\). According to Faraday’s Law, the electrochemical corrosion rate increases linearly with
increasing corrosion current density [13]. The MHG4 alloy demonstrated the highest corrosion resistance of all tested alloys, indicating the inhibition of corrosion with an increasing Ga/Hg ratio. This result is consistent with the fact that Ga is a high hydrogen evolution overpotential element [14].

Alloy MHG4 demonstrated the minimum corrosion current density, and the most positive corrosion potential (Ecorr). Alloy MHG2 demonstrated a more negative corrosion potential and a higher corrosion current density than MHG3, caused by the high activity of Mg3Hg. Mg3Hg could also reduce the formation of a corrosion product film on the alloy surfaces [6]. The passivation of the polarization curves of MHG4 can be observed in Figure 3, passivation disappeared as the Ga/Hg ration decreased.

Table 2. Potentiodynamic polarization curves of experimental results.

|        | Ecorr (V/SCE) | icorr (mA/cm²) | ba (V/decade) | bc (V/decade) |
|--------|--------------|----------------|--------------|--------------|
| MHG1   | -1.767       | 5.23           | 0.180        | 0.589        |
| MHG2   | -1.698       | 3.43           | 0.195        | 0.474        |
| MHG3   | -1.578       | 1.95           | 0.178        | 0.299        |
| MHG4   | -1.437       | 0.025          | 0.071        | 0.106        |

Figure 4 displays the galvanostatic curves of the tested alloys. Experimental current density was 100mA/cm², with an electrolyte of 3.5wt% NaCl. The MHG1, MHG3, and MHG3 alloys reached maximum voltage in 10 seconds, whereas MGH4 obtained maximum voltage in 60 seconds. This result indicates that the activation times of the first three alloys are shorter; thus, the MHG1, MHG2, and MHG3 alloys have been identified as potential anode materials for seawater batteries.

Seawater batteries require negative potential. As the Ga/Hg ratio increases, the electrode potential shifts to less negative values, thus decreasing the driving potential. The MHG4 alloy with a Ga/Hg ratio of 1.12 demonstrated the most positive potential of -1.68V (vs. SCE). Thus, we determined that alloys with a Ga/Hg ratio that exceeds 0.97 cannot meet the functional requirements of a seawater battery anode. The demonstrated electrode potentials of MHG1 and MHG2 were both approximately -1.83V. When the Ga/Hg ratio increases to 0.68, the discharge process of MHG2 became steadier and discharge time increased; this high voltage and short activation time indicate that the MGH2 alloy may be a suitable material for seawater battery anodes.
When the Ga/Hg ratio increases above 0.97, the effect of Ga becomes more apparent as the second phase changes to Mg$_5$Ga$_2$. With an increasing Ga/Hg ratio, the electrode potential shifts, passivation appears and corrosion is inhibited. Contrarily, with a Ga/Hg ratio of less than 0.68, the effect of Hg becomes more apparent as the second phase shifts toward Mg$_3$Hg. As the Ga/Hg ratio increases, the discharge process becomes steadier and the discharge time increases.

4. Conclusion
An increasing Ga/Hg ratio results in the inhibition of second phase Mg$_3$Hg. As the Ga/Hg ratio reaches 0.97, the eutectic phase changes from eutectic α-Mg+Mg$_3$Hg to eutectic α-Mg+Mg$_5$Ga$_2$. The normal eutectic morphology simultaneously transforms to a divorced eutectic structure.

As the Ga content of the alloy increases, the corrosion density decreases, and anode corrosion is prevented. When the Ga/Hg ratio increases above 0.97, the corrosion current density and the discharge voltage decrease, and the activation time increases. With a Ga/Hg ration of less than 0.68, the corrosion current density remains stable, resulting in a steadier discharge process. Results indicate that the Ga/Hg ratio should not exceed 0.68 in order to obtain optimum electrochemical performance.

When the Ga/Hg ratio increases above 0.97, the electrode potential shifts, inhibiting anode corrosion and resulting in passivation. When the Ga/Hg ratio is less than 0.68, the discharge process becomes steadier and the discharge time increases with an increase in the Ga/Hg ration.

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