Effects of Zn on Corrosion Properties of Homogenized Mg-3Sn-1Ca-1Cu Alloy

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Abstract: The effects of 1% Zn on the corrosion properties of homogenized Mg-3Sn-1Ca-1Cu alloys were investigated. The corrosion behavior of homogeneous TXC311 and TXCZ3111 alloys in 3.5% NaCl solution was studied by using a hydrogen evolution test, polarization curve and impedance spectrum, and the corrosion properties of the alloys were discussed with considerations relative to microstructure. The results show that the second phases of TXC311 alloy consist of CaMgSn and Mg$_2$Cu. The corrosion rate is 132 mm·year$^{-1}$. After the addition of 1% Zn element, the grains are significantly refined, the number of Mg$_2$Cu phases is reduced and the MgZnCu phases are formed. The corrosion rate of Mg-3Sn-1Ca-1Cu alloy decreased to 80 mm·year$^{-1}$. TXCZ3111 alloy presents fine grains and a reduced number of Mg$_2$Cu phases, which improve the stability of the corrosion film and reduce the corrosion rate of the alloy. Therefore, the corrosion resistance of TXCZ3111 alloy is much higher than that of TXC311 alloy.

Keywords: Mg-3Sn-1Ca-1Cu alloy; Mg-3Sn-1Ca-1Cu-1Zn alloy; homogenized; corrosion properties

1. Introduction

Magnesium alloys, as the lightest metal structure material, are widely used in the 3C electronics industry, aerospace, transportation and other fields at present due to their high strength and specific stiffness [1]. However, their poor corrosion resistance has seriously limited the practical application of magnesium alloys. There are two methods to improve the corrosion resistance of magnesium alloys [2]. The first is a method of refining the grain and changing the type and distribution of phases by alloying. The other method is to cover the surface of a magnesium alloy by using surface technology such as coating to reduce or eliminate contact between the magnesium alloy and the external environment [3,4]. Generally speaking, the preparation for coating is more complex. In most cases, alloying is popular for improving the corrosion resistance of magnesium alloys.

Due to high solid solubility and significant precipitation strengthening effects, 1–2% Sn forms a Mg$_2$Sn phase with a high melting point in magnesium and its alloys [5]. Therefore, the role of Sn in magnesium alloys has been investigated. For example, Sun [6] found that the addition of Sn can transform microstructures from coarse columnar grains into dendrites and obviously refine the grain. The addition to the alloy of 3% Mg$_2$Sn second phase distributes onto the grain’s boundary, which promotes the generation of cracks. In addition, Sn can also improve the corrosion resistance of magnesium and its alloys. For example, adding 0.5% Sn to AZ91 reduces the corrosion rate of the alloy by 18.2%, which greatly promotes the application of Sn in magnesium alloys [7]. Furthermore, Mg-Sn-Ca alloys have attracted much attention in recent years because of their good heat resistance. After adding Ca elements to magnesium alloys, CaMg$_2$Sn and Mg$_2$Sn form heat-resistant phases and refine grains, which improves high-temperature resistance [8–11]. Some studies indicate that adding Cu elements can improve the castability, ductility and strength of magnesium alloys [12]. The age hardening
The ability of magnesium alloy containing Cu can also be improved by heat treatment [13]. For example, ZK60 alloy with added 0.5%–1% Cu has better mechanical properties after aging treatments [14]. The addition of Cu to Mg-Zn-Cu-Al-Mn high-strength alloys can enhance the ductility of the alloy by forming separate eutectic MgZnCu phases [15]. Although Cu can improve the mechanical properties of magnesium alloys, it can reduce their corrosion resistance. Lotfpour [16] studied the effects of Cu on the mechanical properties and corrosion properties of as-cast Mg 2%Zn alloy. The results show that the tensile strength and elongation were 171 MPa and 15%, respectively, but the corrosion resistance of Mg 2%Zn alloy significantly decreased by adding 0.5% Cu.

Zn, an inexpensive element, can significantly refine the grain and improve the corrosion resistance of magnesium alloys. Ha [17] studied the effects of different Zn contents on the corrosion resistance of Mg-5Sn alloys, and the results show that the addition of Zn improves the corrosion resistance of the alloy. Previous studies have shown that Mg-Sn-Ca alloys are heat-resistant magnesium alloys with potential applications and development value [18,19]. Previous tests show that adding 1% Cu can significantly improve the mechanical properties of Mg-3Sn-1Ca alloy, but it is observed that the corrosion resistance of Mg-3Sn-1Ca-1Cu alloy is poor. Therefore, this study considers adding 1% Zn to improve the corrosion resistance of Mg-3Sn-1Ca-1Cu alloys. The microstructure and corrosion resistance of homogeneous Mg-3Sn-1Ca-1Cu and Mg-3Sn-1Ca-1Cu-1Zn alloys were studied by XRD, OM, SEM, hydrogen evolution tests and electrochemical test.

2. Materials and Methods

In this experiment, Mg-3Sn-1Ca-1Cu and Mg-3Sn-1Ca-1Cu-1Zn alloys were prepared by using industrial pure Mg (99.9 wt.%), pure Sn (99.9 wt.%), Mg 25%Ca master alloy, pure Zn (99.9 wt.%) and pure Cu (99.9 wt.%). The process is as follows: Firstly, the pure magnesium ingots in the iron crucible were melted in a resistance furnace with CO₂ + 0.5% SF₆ gas mixture for protection. After the magnesium ingots were completely melted, the crucible was heated to 750 °C, and then the Cu sheets were added into the melt and stirred homogeneously. The melt was decreased to 710 °C for 10 min for slag removal, and Mg 25%Ca, Sn and Zn were placed into the melt and stirred homogeneously for 2–3 min. Finally, the melt was left to stand for 20 min and then poured into the ϕ65 × 240 mold. After cooling to room temperature, the ingots were homogenized for 400 °C × 24 h. The chemical composition test results of the alloy samples are shown in Table 1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Sn</th>
<th>Ca</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3Sn-1Ca-1Cu (TXC311)</td>
<td>Bal.</td>
<td>3.22</td>
<td>1.04</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>Mg-3Sn-1Ca-1Cu-1Zn (TXCZ3111)</td>
<td>Bal.</td>
<td>3.18</td>
<td>1.04</td>
<td>1.04</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Firstly, the heads of ingots with shrinkage defects (about 80 mm) were removed. The specimens were taken from the center of the ingots by using a wire-cutting machine, as shown in Figure 1. Secondly, the microstructure and phase morphology observations were carried out by utilizing optical microscopy and scanning electron microscopy (SEM-S4800 by Hitachi, Japan) with EDS. Phase identification was performed by using X-ray diffraction (XRD-7000 produced by Shimadzu, Kyoto, Japan).
The specimens were analyzed by conducting immersion and hydrogen evolution reaction tests. They were cut into cubes with dimensions of 10 mm × 10 mm × 10 mm, and then ground with several SiC papers and mechanical polishing. The immersion test was conducted at 25 ± 1 °C in 3.5 wt.% NaCl solution (500 mL) for 24 h, and hydrogen gas was collected with a burette and recorded every 2 h. In order to keep the concentration of the solution stable, the NaCl solution was replaced every 12 h. The samples were taken out and placed into chromate for 10 min of ultrasonic cleaning after corrosion. Each experiment was repeated three times to ensure the accuracy of the data.

The corrosion rate can be expressed as \( P_H (\text{mm/year}) \) and is calculated as follows:

\[
P_H = \frac{8.76 \times 10^4 \times \Delta V \times M}{A \times t \times \rho}\tag{1}
\]

where \( P_H \)—hydrogen evolution corrosion rate, mm·year\(^{-1}\);
\( \Delta V \)—total amount of hydrogen gas during corrosion, mL;
\( M \)—the relationship between the hydrogen precipitation rate and the alloy mass loss rate, 0.001083, g·mL\(^{-1}\);
\( A \)—total surface area of soaked sample, cm\(^2\);
\( t \)—soaking time, h;
\( \rho \)—sample density of weight loss measurement, g·cm\(^{-3}\).

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were acquired by using a standard three-electrode cell electrochemical workstation (CHI660E). The saturated calomel electrode was the reference electrode, the platinum electrode was the auxiliary electrode, and the working electrode was the sample.

In this experiment, the sample was immersed in the solution for 3600 s, and the potentiodynamic polarization curve was tested after the potential was stable. The potential was set to an instantaneous potential ± 0.5 V, and the scanning rate was 1 mV/s. When measuring the electrochemical AC impedance spectrum, the amplitude of the AC signal was 5 mV/s, the scanning frequency range was 100 kHz~0.01 Hz, and the scanning direction was from high frequency to low frequency. Each experiment was repeated three times. The current densities \( i_{\text{corr}} \) and corrosion potentials \( E_{\text{corr}} \) were obtained by conducting graphical Tafel analysis. The relationship between \( i_{\text{corr}} \) (mA/cm\(^2\)) and the electrochemical corrosion rate (mm/year) is described by Equation (2) [20,21].

\[
P_1 = 22.85 i_{\text{corr}}\tag{2}
\]

3. Results and Discussions

3.1. Microstructure Evolution

Figure 2 shows the microstructures and SEM/EDS of the homogenized TXC311 and TXCZ311 alloys. The average grain size of the TXC311 alloy is 449 μm, and the black second phases are well-distributed. After the addition of 1% Zn element, the grain size is obviously refined, and the average grain size is about 286 μm, while the microstructures
show equiaxed grain. With the addition of 1% Zn, the amount of the second phase decreases obviously, as shown in the SEM images. Moreover, energy spectrum results show that the second phase of the TXC311 alloy is composed of strip CaMgSn phase (point A) and spherical Mg$_2$Cu phase (as shown at point B). A small amount of needle-like MgZnCu phase (as shown at point D) is formed in the TXCZ3111 alloy, and the content of Mg$_2$Cu phases decreases. The formation of MgZnCu phase consumes Cu elements in the alloy, resulting in the reduction of Mg$_2$Cu phase. A large number of CaMgSn phases are distributed in both alloys, which is mainly related to the Sn/Ca mass ratio. When the Sn/Ca mass ratio is close to 3, CaMgSn phases mainly exist in TX31 alloys [18].

Figure 2. OM and SEM/EDS images of homogeneous TXC311 and TXCZ3111. (a,b) TXC311; (c,d) TXCZ3111; (e,f) represent point A and point B in (b), respectively; (g,h) represent point C and point D in (d), respectively.

Figure 3 shows the X-ray diffraction (XRD) of TXC311 and TXCZ3111 alloys. It can be seen that both the TXC311 alloy and TXCZ3111 alloy have CaMgSn and Mg$_2$Cu phases. However, no MgZnCu phase was detected in the TXCZ3111 alloy because its amount is so low.
However, no MgZnCu phase was detected in the TXCZ3111 alloy because its amount is so low.

Figure 3. XRD patterns of TXC311 and TXCZ3111 homogeneous alloys.

3.2. Corrosion Properties

Figure 4 shows the macro-photos and SEM images of the two alloys after soaking for 24 h. Compared with Figure 4a,b, it was observed that the surface corrosion of the TXC311 alloy is more severe than that of the TXC3111 alloy, and the corrosion pit can obviously be observed in the TXC311 alloy. As shown in Figure 4c,d, the corrosion pits of the TXZ3111 alloy are relatively shallow, and spherical pitting pits are found in the corroded matrix because the Mg\textsubscript{2}Cu phase has higher potential than that of \(\alpha\)-Mg. Compared with the MgZnCu and CaMgSn phases, Mg\textsubscript{2}Cu preferentially induces matrix corrosion. Therefore, it can be concluded that the addition of Zn reduces the Mg\textsubscript{2}Cu phase of TXC311 alloys, which can effectively improve the matrix’s potential.

Figure 4. Macroscopic and SEM images of homogeneous TXC311 and TXCZ3111 alloys. (a,c) TXC311; (b,d) TXCZ3111.

Figure 5 shows the average hydrogen content and corrosion rate of the TXC311 and TXCZ3111 alloys after soaking for 24 h. It shows the approximate linear relationship
between the amount of hydrogen and the soaking time in the two alloys, which indicates that the amount of hydrogen is almost equal in each time period. From Figure 5a, it can be found that the hydrogen evolution amount of TXC311 and TXCZ3111 alloys is linearly correlated with time. During this time period (0–2 h), the hydrogen evolution of the TXCZ3111 alloy has a nonlinear relationship with time. The corrosion rate of TXC311 and TXCZ3111 alloys are 132 mm·year⁻¹ and 80 mm·year⁻¹, respectively, as shown in Figure 5b. Therefore, the addition of 1% Zn can reduce the corrosion rate of Mg-3Sn-1Ca-1Zn alloys.

Figure 5. Corrosion of homogenized TXC311 and TXCZ3111 alloys by immersion for 24 h. (a) Volume of H₂; (b) corrosion rate.

Figure 6 shows the polarization curves (a), Nyquist plots (b) and Fitting circuit (c) of the TXC311 and TXCZ3111 alloys. Generally speaking, the cathodic polarization curve represents the hydrogen evolution reaction of water reduction, and the anodic polarization curve represents the dissolution of the magnesium matrix. Table 2 shows the fitting data of the polarization curve and impedance spectrum. The corrosion potential of the TXC3111 alloy is slightly higher than that of the TXC311 alloy, and the corrosion current density of the TXCZ3111 alloy is much lower than that of the TXC311 alloy, which indicates that Mg-3Sn-1Ca-1Zn alloys has better corrosion resistance. The corrosion rate calculated by electrochemistry shows a similar trend relative to the immersion test. However, the corrosion rate obtained from the polarization curve is quite different from that calculated from hydrogen evolution because the corrosion rate measured by the polarization curve is suitable for the sample right after being soaked (3600 s), while the corrosion rate measured by the hydrogen evolution method is the corrosion rate after soaking for 24 h. The polarization curve reflects the thermodynamic tendency of corrosion, and the impedance graph (EIS) reflects the kinetic tendency of corrosion. EIS is usually used to reflect the actual corrosion resistance of materials, and the polarization curve is used as a supplemental method [22]. Therefore, in order to further study the corrosion mechanism, the impedance spectra of the two alloys are shown in Nyquist curves, as shown in Figure 6b. The Nyquist curves of both the TXC311 and TXCZ3111 alloys have a high-frequency capacitive reactance arc, a medium-frequency capacitive reactance arc and a low-frequency inductive reactance arc, which indicates that Zn addition does not change the corrosion mechanism. The TXC311 alloy has the largest capacitive arc resistance at any frequency. It can be concluded that the charge transfer resistance and the resistance of the surface film are the highest. The stability of the oxide film is higher than that of the TXC311 alloy in the dynamic corrosion process, which can hinder the corrosion of the α-Mg matrix and improve the corrosion resistance of the alloy [23]. Equivalent circuit fitting was performed on the impedance spectra of the TXC311 and TXCZ3111 alloys, as shown in Figure 6c, and specific parameters are shown in Table 2. Rs is the solution resistance, Rct is the charge transfer resistance and Rf is the surface film resistance. Rf and L in the series circuit represent the rupture of the partial oxide layer in the alloy’s surface, which is used to fit the low-frequency inductive reactance arc in the equivalent circuit. The constant phase angle element CPEdl is connected in parallel with resistance Rf to fit the high-frequency capacitive reactance arc, and the normal-phase angle element CPEf and resistance Rf are used in parallel to
fit the intermediate-frequency capacitive arc in the equivalent circuit. As observed from Figure 5b, the simulation results of equivalent circuit are in accordance with the experimental results. With increasing values of \( R_f \) and \( R_L \), the corrosion resistance of the films increases. Table 2 shows the results that \( R_L(\text{TXCZ3111}) > R_L(\text{TXC311}) \) and \( R_t(\text{TXCZ3111}) > R_t(\text{TXC311}) \). Therefore, it can be concluded that pitting corrosion occurs on the surfaces of TXC311 and TXCZ3111 alloys during the corrosion process, but the corrosion product film induced destruction, and the extent of pitting corrosion of the TXCZ3111 alloy is less than that observed in the TXC311 alloy. Therefore, the TXCZ3111 alloy has higher corrosion resistance than that of the TXC311 alloy.

![Figure 6. (a) Polarization curves; (b) Nyquist plots; (c) Fitting circuit.](image)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ecorr/V</th>
<th>( \text{Ion/mAh} \cdot \text{cm}^{-2} )</th>
<th>( R_L ) (mm²/year)</th>
<th>CPE(_{dl})</th>
<th>( R_L ) (cm²)</th>
<th>( R_f ) (cm²)</th>
<th>L (H cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TXC311</td>
<td>1.679 ± 0.029</td>
<td>98.9 ± 10.2</td>
<td>2.03 ± 0.23</td>
<td>2.61 ± 0.34</td>
<td>6.68 ± 1.35</td>
<td>0.89 ± 0.02</td>
<td>4.67 ± 0.23</td>
</tr>
<tr>
<td>TXC3111</td>
<td>-1.457 ± 0.053</td>
<td>45.7 ± 5.3</td>
<td>0.98 ± 0.03</td>
<td>2.80 ± 0.25</td>
<td>6.63 ± 0.36</td>
<td>0.87 ± 0.02</td>
<td>3.10 ± 0.15</td>
</tr>
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The hydrogen evolution test shows that the corrosion rate of the TXCZ3111 alloy is lower than that of the TXC311 alloy. As observed from the Tafel polarization curve, the corrosion current density of the TXC3111 alloy decreases, and the corrosion potential increases. The obvious passivation zone can be also observed in the cathode curve, which indicates that the more stable corrosion film forms on the surface of the TXZ311 alloy. It hinders the formation of corrosion pits, as shown in Figure 4.

The corrosion resistance of magnesium alloy is mainly attributable to grain size, the homogeneity of microstructure and defect density [24]. The results show that smaller grain size can improve corrosion resistance. In addition, second-phase particles also play an important role in the corrosion behavior of magnesium alloys. In general, the self-corrosion potential of the second-phase particles is higher than that of the magnesium matrix [2,25]. Therefore, when the magnesium alloy is immersed in 3.5 wt.% NaCl solution, the corrosion potential of the second-phase particles is higher than that of the magnesium matrix, resulting in rapid corrosion of the magnesium matrix around the second phase [26]. The corrosion mechanism of TXC311 and TXCZ3111 alloys is shown in Figure 7. The grain size of the TXCZ3111 alloy (286 µm) is obviously smaller than that of the TXC311 alloy (449 µm), and more grain boundaries can reduce the corrosion rate of the alloy in a physical shielding role. Secondly, the subsequence of corrosion resistance ability is as follows: CaMgSn > MgZnCu > Mg₃Cu. Meanwhile, the Mg₃Cu phase has a higher potential (−1.69 V) than that of α-Mg. Therefore, the Mg₃Cu phase and α-Mg, as cathodes and anodes, respectively, accelerate the corrosion of alloys through the process of micro-galvanic corrosion [27]. Therefore, the corrosion resistance of the TXC311 alloy is poor due to its large number of Mg₃Cu phases. After adding Zn elements, the volume fraction of the second phase is significantly reduced. MgZnCu phases can decrease the number of Mg₃Cu phases, which improves the corrosion resistance of the alloy [28].
4. Conclusions

The microstructure and corrosion properties evolution in homogenized TXC311 alloy and TXCZ3111 alloy are studied in this paper, and the following conclusions were obtained:
TXC311 alloys contain a large number of CaMgSn and Mg$_2$Cu phases. After adding 1% Zn, the grain size of TXC311 alloy decreases significantly, and the MgZnCu phase is formed.

TXC311 alloys have poor corrosion resistance, which is due to the Mg$_2$Cu phase possessing a higher potential (−1.69 V) than that of α-Mg. The addition of Zn can effectively reduce the corrosion rate of TXC311 alloy, which can be attributed to grain refinement and the reduction of the Mg$_2$Cu phase. In addition, the formation of the MgZnCu phase also plays a positive role in the corrosion resistance of TXC311 alloys. Therefore, the corrosion resistance of TXCZ3111 alloys is much higher than that of TXC311 alloys.

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