Electrochemical and corrosion behaviors of pure Mg in neutral 1.0% NaCl solution

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Abstract: The corrosion behaviors and corresponding electrochemical impedance spectroscopy (EIS) and polarization curves of pure Mg in neutral 1.0% NaCl solution were investigated. The fractal dimension of EIS at different time was studied. The corrosion process and EIS evolution are divided into three stages. In the initial stage, EIS is composed of two overlapped capacitive arcs, the polarization resistance and charge transfer resistance increase rapidly with immersion time, and the corrosion rate decreases. Then, two well-defined capacitive arcs appear, and the charge transfer resistance and corrosion rate remain stable. After a long immersion time, inductive component appears in a low frequency range, the charge transfer resistance decreases and the corrosion rate increases with the immersion time. The fractal dimension obtained from the time records of EIS seems to be a promising tool for the analysis of corrosion morphology because of its direct relationship with the metal surface.

Key words: pure Mg; corrosion; electrochemical impedance spectroscopy (EIS); fractal dimension

1 Introduction

Mg is one of the most active and lightest metals. In particular, its high specific strength and rigidity, high damp and castability, marketable lowering energy exhaust and good electronic and thermal conductivity make Mg and its alloys extremely attractive for applications requiring light mass, such as aerospace and transportation. However, low corrosion resistance is a major handicap to their application growth, despite their other desirable physical properties [1, 2]. Their high reactivity or low electrode potential easily leads to corrosion even in the atmosphere. Thus, in order to achieve long-term performance of Mg and its alloys, it is imperative to obtain a thorough understanding of their corrosion process and the associated electrochemical behaviors [3–6]. Pure Mg is an ideal sample to study the electrochemical evolution during the corrosion process and the relationship between the electrochemical characteristics and the corresponding corrosion features.

Generally, it is well accepted that Mg is easily oxidized to form a thick hydroxide film when it is in contact with humid air or water [7, 8]. The high reactivity of Mg has a detrimental effect on its protective coating qualities, such as adhesion, pore density and uniformity. It is therefore important to get information about its hydroxide film growth, while it is also necessary to understand the corrosion mechanism of the Mg in aqueous solutions. Recently, there have been several studies on the corrosion behavior of pure Mg and Mg alloys in humid air and water [9–12]. These studies showed that the surface hydroxide films grew rapidly after immersion in solutions. Some other previous studies also revealed that a film with partial protectiveness might form on Mg surface in Na2SO4 solution [13]. However, the effect of such a film on the corrosion behavior of Mg needs to be clarified in more details.

It was reported that the fractal-based self-similarity
was useful in the analysis of electrochemical and corrosion process [14]. Fractals are mathematical sets with a high degree of geometrical complexity, which can model many kinds of time series [15]. SAPOVAL et al [16] suggested why the fractal dimension could be used to characterize the EIS of electrodes with different structures and also showed that the impedance varied as a function of the fractal dimension. ZHAO et al. [17] also used fractal dimension associated with EIS to analyze the corrosion morphology of pure Mg.

The purpose of this study is to investigate the evolution of the electrochemical features and examine the influence of the formed hydroxide films on the corrosion behaviors of pure Mg through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements in conjunction with the scanning electron microscopy (SEM). Furthermore, the fractal study of EIS is applied to analyzing and characterizing the corrosion process of pure Mg, trying to establish the relationship between the fractal dimensions and corrosion features.

2 Experimental

The rod specimen of pure Mg with an exposed area of 0.5 cm² was used, and its composition was 99.99% (mass fraction) Mg. The rod specimen was sequentially polished with silicon carbide paper from 400# to 800# and 2.5 μm-diamond paste, rinsed with twice-distilled water, washed with acetone, rinsed with twice-distilled water again and then dried in the air. The corrosion medium used in this study was 1.0% (mass fraction) NaCl solution, which was prepared by analytical grade NaCl and deionized water. The pH value of the solution was adjusted to pH=7.03.

The electrochemical measurements were performed in a three-electrode electrochemical cell. The magnesium rod was the working electrode. The auxiliary electrode was a large platinum sheet and the reference electrode was a saturated calomel electrode (SCE). The reference electrode was placed outside the cell and connected to the NaCl solution through a Luggin capillary and a salt bridge. All potentials presented in this study were referred to SCE. All electrochemical measurements were carried out at about 30 °C.

Polarization curves at various immersion time were measured using a Powerlab/4sp recorder with a GP amplifier. After the measurement of open circuit potential (\(\phi_{ocp}\)), all polarization curves were recorded potentiodynamically with a sweep rate of 0.5 mV/s, and the potential range of 250 mV to −200 mV (referred to \(\phi_{ocp}\)) was selected.

The EIS experiment at different immersion time was performed using an IM6e (ZAHNER, Germany) electrochemical workstation driven by a computer and carried out with an amplitude of 10 mV (referred to \(\phi_{ocp}\)) in a frequency range of 0.01 Hz to 10 kHz. Six points per decade of frequency were recorded. Each EIS experiment was performed after the \(\phi_{ocp}\) reached steady. Then, an equivalent circuit was constructed, and a Zview software 2.7 (Scribner Associates Inc) was used to analyze the EIS results.

The Mg rods were immersed in the 1.0% NaCl solution for different time. Then, they were removed out from the solution. After drying, the corrosion morphology was observed with a SEM (SIRION).

3 Results and discussion

3.1 Polarization behaviors

Figure 1 presents the steady-state polarization curves of pure Mg at different immersion time in the 1.0% NaCl solution. First of all, all these polarization curves have similar shapes and exhibit Tafel behaviors in both anodic and cathodic branches. The corresponding corrosion potential (\(\phi_{corr}\)), polarization resistance (\(R_p\)) and corrosion current density (\(J_{corr}\)) are listed as a function of immersion time in Table 1. It is found that both the corrosion current density \(J_{corr}\) and polarization resistance \(R_p\) depend strongly on the immersion time. The polarization resistance \(R_p\) increases with extending immersion time from 1.7 h to 8.7 h. Correspondingly, the corrosion current density \(J_{corr}\) is decreased. This should be associated with the formation of hydroxide film with partial protectiveness. After that, the polarization resistance \(R_p\) remains stable and then decreases a little as the immersion time extends to about 92 h, while the

![Fig. 1 Potentiodynamic polarization curves of pure Mg in 1.0 % NaCl solution for different immersion time](image-url)
Table 1 Fitted corrosion parameters of pure Mg in 1.0% NaCl for different immersion time

<table>
<thead>
<tr>
<th>Immersion time/h</th>
<th>$R_p$/kΩ</th>
<th>$J_0$/μA·cm$^{-2}$</th>
<th>$\varphi_{corr}$ (vs SCE)/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>7.653</td>
<td>8.577</td>
<td>−1.5772</td>
</tr>
<tr>
<td>8.7</td>
<td>8.798</td>
<td>4.876</td>
<td>−1.5852</td>
</tr>
<tr>
<td>21</td>
<td>8.634</td>
<td>5.234</td>
<td>−1.6073</td>
</tr>
<tr>
<td>92</td>
<td>8.329</td>
<td>4.938</td>
<td>−1.6129</td>
</tr>
</tbody>
</table>

corrosion current density $J_{corr}$ remains steady. Visual observation after the potentiodynamic polarization curve measurement reveals that the electrode surface is severely corroded and presents black and much uneven.

3.2 Electrochemical impedance spectroscopy

The EIS characteristic curves of pure Mg in 1.0% NaCl solution for different immersion time are shown in Figs. 2–4. The corrosion process of pure Mg can be

![Fig. 2 Nyquist (a) and Bode (b) plots of pure Mg in 1.0% NaCl solution for immersion time of 40 min and 9 h](image1)

![Fig. 3 Nyquist (a) and Bode (b) plots of pure Mg in 1.0% NaCl solution for immersion time of 10 h, 48 h and 60 h](image2)

![Fig. 4 Nyquist (a) and Bode (b) plots of pure Mg in 1.0% NaCl solution for immersion time of 68 h, 101 h and 120 h](image3)
divided into three sequential stages according to the characteristics of EIS data, including the number of time constant, the phase angle peak and trend of the total impedance.

Figure 2 shows the EIS plots of pure Mg in the 1.0% NaCl solution during the first immersion stage of 40 min and 9 h. It is seen that the Nyquist plots are characterized by only one visual capacitive arc above the real axis, and the radius of the capacitive arcs decreases with the immersion time. However, the difference between the experimental data and the fitted data leads to the derivation of at least two time constants [18]. When this difference shows a periodicity, it means that not all the time constants are taken into account. Therefore, at the immersion time of 40 min and 9 h, the visual capacitive arcs above the real axis in Fig. 2 should be composed of two time constants, or two capacitive arcs are almost overlapped completely.

In the second stage, two capacitive arcs are clearly observed, as shown in Fig. 3. After 10 h of immersion in the 1.0% NaCl solution, another capacitive arc is easily seen in the low frequency range, illustrating that the surface of the Mg electrode is not homogeneous. With the extension of the immersion time to 48 h and 78 h, the low-frequency capacitive arc emerges gradually as another well-defined capacitive loop above the real axis. These two visual capacitive loops can be considered two constants, which also can be seen from double phase angle peaks detected in the Bode diagram (Fig. 3(b)).

In the third stage, inductive components are observed in the EIS plots, as shown in Fig. 4. After 68 h of immersion in the NaCl solution, we can see two well-defined capacitive loops above the real axis at high and medium frequencies, followed by inductive component in the low-frequency range. The inductive behavior is often explained by the relaxation phenomenon of reaction intermediates [19]. In fact, the origin of inductive features in the electrode impedance is numerous. For example, when the potential shifts towards more anodic direction or time dependent change of the electrode interface promotes the dissolution reaction, the inductive feature is expected. As for Al alloys, KEDDAM et al [19] and CAO et al [20] indicated that the inductive behavior is more likely promoted by the weakening of the protectiveness of their oxide film. Because in this case, a hydroxide film with partial protectiveness is formed on the Mg surface, it is believed that the inductive phenomenon is associated with the weakening of the effectiveness of this hydroxide film.

Based on the above observation, the number of time constants involved in the whole corrosion process of pure Mg in the 1.0% NaCl solution is determined, and an equivalent circuit model (Fig. 5) with two time constants is constructed to characterize the corrosion process [21].

In Fig. 5, \( C_c \) represents the capacitance of the Mg substrate/film and film/electrolyte, and \( C_{dl} \) is the double-layer capacitance; while, \( R_c \), \( R_p \) and \( R_t \) are the electrolyte resistance, the hydroxide film resistance and the charge transfer resistance, respectively.

\[
\text{CPE} = \frac{1}{Y_0(j\omega)^n}
\]

where \( Y_0 \) is a general admittance function; \( j \) is the complex operator \((-1)^{1/2}; \omega \) is the angular frequency; \( n \) is an empirical exponent. The presence of a CPE has often been explained by dispersion effects that may be caused by microscopic roughening of a surface, which, in turn, is related to surface preparation or localized corrosion [22].

Figure 6 shows the relationship between the fitted charge transfer resistance \( R_t \) and the immersion time. It is seen that \( R_t \) increases rapidly during the first 7 h of immersion, which means that the corrosion rate decreases during this period. This is consistent with the polarization result that the polarization resistance \( R_p \) increases with extending immersion time from 1.7 h to 8.7 h (Table 1). Then, during the immersion period from 7 h to about 60 h, \( R_t \) remains at a high stable value, indicating a steady and low corrosion rate. This is also consistent with the polarization measurement. Over about 60 h of immersion, \( R_t \) begins to decrease, indicating that the corrosion rate increases. During the immersion period, the hydroxyl produced on cathode reacts with the Mg atoms and results in the rapid growth of a hydroxide film. This film plays an extremely important role in the electrochemical corrosion process of pure Mg, which supplies a partial protection to the tectorial surface, and results in the rapid increase of polarization resistance \( R_p \) (Table 1) and charge transfer resistance \( R_t \) during the initial stage. As the growth of this protective film results in the balance of the reaction resistance value, the polarization resistance \( R_p \) (Table 1) and charge transfer resistance \( R_t \) remain stable during the second immersion stage. The peak of low-frequency phase angle also becomes more and more distinct due to this film. However, this film is much loose and cracks will form after a long time, so the chloride ions can
penetrate it down to the Mg substrate. Therefore, inductive component appears, the charge transfer resistance $R_t$ begins to decrease and the corrosion rate increases during the third stage after about 60 h of immersion.

![Graph showing relationship between $R_t$ and immersion time]

**Fig. 6** Relationship between $R_t$ and immersion time

Figure 7 shows the relationship between the fitted capacitance $C_{dl}$ and immersion time. The capacitance $C_{dl}$, which may be originated from the formation of the corrosion products (the hydroxide film), increases rapidly during the first 22 h of immersion (Fig. 7). Then it decreases followed by keeping stable. This change trend of $C_{dl}$ should be due to the even formation and thickening of the hydroxide film with partial protection. After 117 h of immersion, $C_{dl}$ increases a little again during the remaining period, which may be due to the formation of the cracks on the hydroxide film and the penetration of the aggressive chloride ions to the substrate under the film.

![Graph showing relationship between $C_{dl}$ and immersion time]

**Fig. 7** Relationship between $C_{dl}$ and immersion time

3.3 Corrosion morphologies

Figure 8 shows the typical corrosion morphologies of pure Mg immersed in the NaCl solution for different time. It can be seen that after 10 min of immersion in the NaCl solution, a few pits and cracks can be observed despite the whole surface are relatively smooth (Fig. 8(a)). The uneven surface is originated from the attack of the chloride ions and dissolution of Mg. With the extension of the immersion time, some pits tend to develop, and corrosion product (hydroxide film) is observed on the surface (Fig. 8(b)). But generally, the lifetime of these pits is short, and these pits are shallow.

![SEM morphologies of pure Mg immersed in 1.0% NaCl solution](image)

**Fig. 8** SEM morphologies of pure Mg immersed in 1.0% NaCl solution for 10 min (a), 1 h (b), 10 h (c) and 68 h (d)
When anodic and cathodic reaction rates approach to equal, the uniform corrosion is set up. The corrosion products (hydroxide film) accumulate (Fig. 8(c)) and even cover the whole area of the electrode surface. This hydroxide film inhibits the diffusion of the aggressive chloride ions from the solution to the substrate, resulting in the increase of $R_p$ and $R_t$. After 68 h of immersion, the thickness of the corrosion product film increases and produces enough stress, resulting in its cracks (Fig. 8(d)) and also the appearance of the inductive component in low-frequency range (Fig. 4).

3.4 Fractal analysis

In CPE component of the equitation circuit, the exponent $n$ is a unitless parameter. If $n$ is equal to 1, the corresponding CPE represents for an ideal capacitor. In most real systems, ideal capacitive behavior is not observed due to surface roughness, or other effects that can cause uneven current distributions on the electrode surface. The value of $n$ can be interpreted as an indication of the inhomogeneity degree of the metal surface. This inhomogeneity degree is associated with the fractal dimension of the surface. Taking into account the depression degree of the capacitive arc in the Nyquist plots, it is possible to determine the fractal dimension of the electrode surface by means of the two following equations

$$D_a = 3 - n$$

$$D_b = \frac{1}{n} + 1$$

where $D_a$ and $D_b$ are the fractal dimensions of the surfaces, which can vary from 2 for a surface completely smooth, to value close to 3 for a rough surface; $n$ is the fitted power exponent of CPE in the high frequency range.

Figure 9 shows the fractal dimensions calculated using above two equations as a function of immersion time. It is clearly seen that these two parameters $D_a$ and $D_b$ display a same trend. The fractal dimensions increase rapidly during the initial immersion period, which means that the surface roughness increases quickly. This is due to the attack of the aggressive Cl$^-$ ions and dissolution of Mg. After that, the corrosion rate is decreased, the anodic and cathodic reactions approach equal, the increase rates of both $D_a$ and $D_b$ are slowed down and then the fractal dimension remains a comparative stable value for about 30 h. After about 60 h of immersion, because of the cracking of the film covering on the electrode surface, new anodic zones are produced, and the surface roughness increases again, leading to the increase of fractal dimensions.

4 Conclusions

1) The EIS evolution of pure Mg in 1.0% NaCl solution is divided into three stages. During the initial stage, EIS is composed of two overlapped capacitive arcs; as immersion time is extended, two well-defined capacitive arcs appear; further extension of immersion time causes the appearance of another inductive component in low frequency range.

2) During the initial stage, the polarization resistance and charge transfer resistance increases rapidly, and the corrosion rate decreases, due to the rapid formation of hydroxide film with partial protectiveness. Then the charge transfer resistance and corrosion rate remain stable. After a long immersion time, due to the formation of cracks on the hydroxide film, the charge transfer resistance decreases, and the corrosion rate increases.

3) The fractal dimension obtained from the time records of EIS seems to be a promising tool for the analysis of corrosion morphology because of their direct relationship with the fractal dimension and the metal surface.

References

纯镁在1.0%NaCl中性溶液中的腐蚀与电化学行为

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摘 要: 研究纯镁在1.0%NaCl中性溶液中的腐蚀行为及其相应的电化学阻抗谱(EIS)和极化曲线，探讨不同时间段 EIS 的分形维数。结果表明，腐蚀过程及相应的 EIS 发展可分为 3 个阶段。初始阶段，EIS 由 2 个重叠的容抗弧组成，相应的极化电阻及电荷转移电阻随着时间的延长而快速增加，而腐蚀速率则降低。而后，EIS 图谱上出现 2 个容易辨认的容抗弧，电荷转移电阻及腐蚀速率基本保持稳定。长时间浸泡后，EIS 图谱中低频部分出现感抗成分，电荷转移电阻降低，而腐蚀速率增加。EIS 分形维数与材料表面形貌直接相关，将是分析腐蚀形貌极有应用的工具。

关键词: 纯镁；腐蚀；电化学阻抗谱(EIS)；分形维数

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