Corrosion Behavior of Chemical Oxidation Film of Magnesium Alloy in NaCl Solution

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Abstract. Magnesium alloy chemical oxidation is a commonly used conductive anti-corrosion treatment method for aerospace. In order to study the corrosion resistance of its chemical oxide film in the coastal launch site and evaluate the impact of the marine environment on its surface film performance, the corrosion properties of magnesium specimens were studied in 3.5% NaCl solution. The corrosion characteristics with different immersion time were characterized by using scanning electron microscopy, energy spectroscopy and electrochemical methods. The corrosion mechanism was discussed. The results showed that as the immersion time increases, corrosion starts from pitting. The pit spreads to the morphology of multi-pronged extension cracks and then continues to deepen and widen, gradually covers the entire surface of the specimen. The corrosion products are mainly composed of magnesium and oxygen. The electrochemical results show that as the corrosion time increases, the corrosion rate increases from 0h to 12h, which the I_{corr} increases and the reaction resistance decreases. However, as the corrosion products cover the surface which prevents the corrosion expanding, the V_{corr} trends to forward shift and reaction resistance increases.

1. Introduction
As low density and high specific strength, the widespread use of Mg alloys is important to aerospace lightweight [1, 2]. To satisfy the application requirements of the space environment, functional treatments on Mg alloys, such as thermal control and conductive treatment, have become one of the necessary issues [3-5]. However, due to the electrochemical activity of Mg, Mg alloys are prone to corrosion, especially in Wenchang Spacecraft Launch Site. In this case, the thermal control and corrosion protection should be considered together [6, 7]. In order to protect Mg alloys from corrosion, nickel plating, aluminum plating, natural anodized, chemical oxidation and micro-arc oxidation will be used in this field [8-10].

Chemical oxidation can improve the corrosion resistance of Mg alloys. Shao et al. [11] found that the formation of Mo on the surface of Mg alloys after chemical oxidation. It can significantly improve the corrosion resistance. Through the Ppy chemical oxidation, Huang et al. [12] found that Mg alloys showed positive shift of 110 mV, and the current density was reduced by about 2 orders of magnitude. Without Cr and P, Xu et al. [13] produced oxide film of 2 to 3 μm by the environment friendly chemical oxidation method. The corrosion resistance rate of the film in 3% NaCl solution was only 1/15 of Mg alloy substrates. On the ZM5 Mg alloy surface, Wang et al. [14] used black chemical oxidation to form a film, which had uniform blackness, densed film and good corrosion resistance performance.

In this work, we have used Mg alloy as chemical oxidation sample, studied the corrosion resistance and the process of corrosion evolution in 3.5wt% NaCl. The performance of sample in different
corrosion time were analysed by electrochemical methods, combined with the corrosion morphology, the corrosion evolution mechanism was also studied.

2. Experimental Section

2.1. Experimental Sample and Procedure
The MB15 alloy was used as experimental sample. The element content was given in table 1 cut into 40mm×40mm×2mm. After turn-milling, MB15 was prepared by degreasing, activation pre-treatment and chemical oxidation. The sample is sealed and protected by chloroprene rubber, leaving only the (40×40) area as the experimental and observed surface. Soaked these samples in 3.5% NaCl solution at room temperature with different intervals (1h, 3h, 6h, 9h, 12h, 18h, 24h). After that, took out the samples and dried it for observation. Finally, samples were cut off to cross-section, and we observed the corrosion characteristics. At the same time, we perform the parallel samples to do electrochemical experiments.

Table 1. The element content of MB15 (wt.%).

| Element | Mg  | Al  | Mn  | Si  | Zn  | Zr  |
|---------|-----|-----|-----|-----|-----|-----|
| Content/% | 92.11 | 0.19 | 0.02 | 0.01 | 4.86 | 2.69 |

2.2. Characterization
After immersion, the sample was dried and observed by the metallurgical microscope (MO). The surface morphology and elements of the sample were observed by CS3400 scanning electron microscope (SEM). At room temperature, the electrochemical impedance spectroscopy (EIS), polarization characteristics and cyclic voltammetry in 3.5wt.% NaCl solution of were tested in different immersion time by using IM6 electrochemical equipment. The experiment used a three-electrode system, a saturated calomel (SCE) electrode as reference electrode, a Pt electrode as counter electrode, the magnesium alloy chemical oxidation sample as working electrode, and the sample exposure area was 1 cm². The test sinusoidal signal disturbance voltage amplitude of EIS is 10 mV, frequency range is 100 kHz ~10 mHz; polarization curve test range is -0.5 V ~ +0.5 V (vs. OCP), scan rate is 5 mV/s, the range of cyclic voltammetry test voltage is -0.25 V ~ +0.25 V (vs. OCP), and the scan rate is 5 mV/s.

3. Results and Discussion

3.1. Corrosion Morphology Analysis
The corrosion MO morphology was shown in figure 1, which shows that all samples in different immersion time in NaCl solution. With the increase of the immersion time, the initial corrosion morphology appears on the surface, which is mainly superficial striated morphology (1h). And then, it is gradually transformed into typical filamentary corrosion morphology (3-6h) such as dendritic multi-forked extension cracks. Corrosion solution gathering around the cracks, the corrosion mainly corrodes along the dendritic cracks, causing the corrosion to extend in depth along the original corrosion marks, and the corrosion cracks become wider and longer than before (12-18h), and finally forms a comprehensive corrosion on the sample surface.

To further analyse the evolution of the microscopic corrosion morphology, the SEM morphology of the sample corrosion with the immersion time is shown in figure 2. After immersed in the NaCl solution, the oxide film of surface quickly appeared micro cracks, and the film layer is partly damaged, showing a grid-like morphology (1h), and then gradually cracked, formed pitting pits (3h). As the immersion time increases, the corrosion corrodes along the pits and bulging cracks to the substrate (12h), and the corrosion products show fluffy morphology (18h), finally large corrosion pits are formed due to the deep development of corrosion.
The results of EDS and element content of magnesium alloy samples in NaCl solution for different corrosion times are shown in figure 3. The surface is mainly contained Mg, Al and Cr oxides when there is no corrosion (0h), indicating that a Cr-containing oxide film is formed on the surface of the magnesium alloy. As the corrosion progresses, the Mg content gradually decreases. However, the O content increases gradually, which indicates that the magnesium oxide continues form on the surface. Cl presents on the surface of all samples immersed in the solution, while the Cr content on the surface first increases and then decreases. The oxygen content of the corrosion products (region B and region D) is significantly higher than that of the non-corrosion region (region C), while the aluminum content
in the corrosion product region gradually reduces with the extension of the corrosion time, which indicates that the corrosion product is mainly magnesium oxide.

![Figure 3. EDS results of specimens with different immersion time.](image)

In order to further analyse the corrosion expansion morphology, the interface morphologies of the samples at different corrosion time are shown in figure 4. After being immersed in NaCl solution, pitting corrosion quickly appears on the surface of the sample (1h). The initial stage of pitting corrosion is faster than that of lateral expansion (3h), and many deep pit-like pits appear. During the corrosion progresses, the corrosion pits of surface gradually expand (6h), and then the corrosion develops forward two directions. One is the surface corrosion products loosed and exfoliated, forming a rugged topography. While the pitting corrosion continues to expand in depth, forming a continuous corrosion, which peeled from surface.

3.2. Electrochemical Performance Analysis
The open circuit potential of the sample with different immersion time is shown in figure 5. As the immersion time increases, it appears positive shift of the open circuit potential. This is mainly because after the Mg alloy corroded, the corrosion products hinder the contact between the solution and the surface of the Mg alloy, resulted in a positive shift of the corrosion potential.
Figure 4. Cross section morphologies of specimens with different immersion time.

Figure 5. Open circuit potential (OCP) of specimens with different immersion time.

The EIS and fitting results for different immersion time of all samples are shown in figures 6, 7 and table 2, respectively. As the immersion time increases from 0 h to 12 h, the reaction resistance decreases from 1684 ohm to 812.9 ohm, indicating that the corrosion resistance of the sample decreases and the corrosion rate increases. After 12-24 h later, the reaction resistance increases from 812.9 ohm to 972.2 ohm, and the corrosion resistant performance of surface is enhanced. Conductive and anti-corrosion oxide film of Mg alloy still has a certain blocking effect in the film layer for 0-6 h soaked. The corrosion rate increases, which lead to the disappearance of reaction capacitance and the reaction resistance decreases for 6-12 h. The corrosion product covered on surface slows down corrosion for 12-24 h, which increases the reaction resistance. However, the capacitive reactance characteristics of the sample surface disappear, indicating that the reaction layer or corrosion product layer weakens the hindrance of the solution.
The polarization curves for different immersion time are shown in figure 8, and the self-corrosion potential and self-corrosion current obtained by fitting the linear polarization zone given in table 3. Compared with the non-immersed sample, the immersed sample has a larger corrosion current, indicating that the immersion reduced the corrosion resistance of the film. When corrosion occurs, the potential of self-corrosion positive shift compared to the original sample. The corrosion potential for 24 h immersion obvious positive shift to -0.935 V, which mainly affects by the coverage of corrosion products [15]. As the immersion time is prolongs, the corrosion rate and the self-corrosion current of the sample for 1-12 h increase, and the reaction resistance decreases. With the coverage of corrosion products, the self-corrosion potential increases for 12-24 h, and the self-corrosion current decreases slightly. The increasement of reaction resistance indicates that the corrosion resistance is slightly improved.
Figure 8. Tafel results of specimens with different immersion time.

Table 3. Fitted data of Tafel results.

| Time (h) | 0   | 1   | 3   | 6   | 12  | 18  | 24  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| \(V_{\text{corr}}\) (V) | -1.241 | -1.275 | -1.185 | -1.204 | -1.181 | -1.221 | -0.935 |
| \(I_{\text{corr}}\) (A/cm²) | 4.53×10⁻⁶ | 8.91×10⁻⁶ | 9.15×10⁻⁶ | 5.27×10⁻⁵ | 8.44×10⁻⁵ | 5.37×10⁻⁵ | 5.05×10⁻⁵ |

The main electrochemical reaction process of Mg alloys is given as follows:

Anode: \(Mg = Mg^{2+} + 2e\)

\(Mg(s) + 2OH^- = Mg(OH)_2 + 2e\)

Cathode: \(2H_2O + 2e = H_2(g) + 2OH^-\)

The initial stage of corrosion initiation (0-3h) is mainly due to the electrochemical inhomogeneity of the Mg alloy surface, especially the Cr-poor and Mg-rich areas are prone to pitting corrosion due to the micro-battery effect. Because the oxide film layer is thin, the inner layer had a certain protective effect during only 1 h (self-corrosion potential and current are close to those of the sample of 0h). As the immersion time increased, the corrosion tip is more likely to form a micro-battery to accelerate the reaction due to the liquid-solid interface, hence pitting corrosion continued to develop in depth [16].

With the progress of the reaction and the corrosion development process (3-12h), the corrosion products gradually increase and prevent the enter of Cl ions. The EDS result indicates that the Cl ion concentration in the corrosion products is lower than the edge of the pit, thus the edge of the pits is more prone to corrosion, so that the corrosion spreads more quickly along the filamentous morphology. At the same time, further deep corrosion occurs. The corrosion rate increases due to the numerous filamentary corrosion tips.

After the formation of corrosion products, the corrosion is stable and extended (12-24h). The corrosion products gradually increase and cover the surface of the sample, reducing the electrochemical activity of the Mg alloy surface. The corrosion rate remains relatively stable, but the electrochemical activity slightly decreases, the corrosion products and the capacitive resistance characteristics of the reaction disappear, and the corrosion expands in the depth and surface at the same time.

4. Conclusion

In this work, we studied the corrosion resistance of Cr-containing conductive anti-corrosive of Mg oxide alloy in 3.5% NaCl solution, and the conclusions as follows:

(1) The corrosion of Mg alloy starts from pitting corrosion, gradually expands in depth in the early stage, forms deep pits, and then gradually develops into multi-pronged filiform corrosion. In the later
stage, the filiform continues to spread and deepen under the corrosion reaction, gradually covers the entire sample surface.

(2) Mg alloy conductive anti-corrosive oxide film still has a certain barrier effect for 0-6 h. When the soaking time is 6-12 h, the corrosion rate increases, which lead to the disappearance of reaction capacitance and the reaction resistance decreases. When the immersion time was 12-24 h, the corrosion product covers on the surface, which slows down the corrosion and increases the reaction resistance.

(3) As the immersion time of Mg alloy in NaCl solution increases, the corrosion rate and the self-corrosion current of 1-12 h sample increases, and the reaction resistance decreases. With the coverage of corrosion products, the self-corrosion potential of 12-24 h sample increases, the self-corrosion current decreases slightly, and the reaction resistance increases, indicating that the corrosion resistance is slightly improved.

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