Effect of Trace Ca on the Corrosion Resistance of ZA124 Magnesium Alloy

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Abstract. The effect of trace Ca addition on corrosion resistance of ZA124 magnesium alloy was studied. The results showed that the effect of adding 0.3% Ca on the refinement of the microstructure of the alloy was obvious, in which the reticular transformation was fine and intermittent or strip-like, and no new phase was formed. With the addition of Ca, the corrosion rate and current density of the alloy in 3.5% NaCl solution decreased, which improved the corrosion resistance of the alloy. When the calcium content was 0.3%, the alloy had the best corrosion resistance.

1. Introduction
Magnesium alloy has the advantages of small density, high specific strength, high specific stiffness, strong liquid filling capacity, non-toxic and easy recovery. It is widely used in automobile, rail transit, aerospace, biomedicine and other fields[1]. The standard electrode potential of magnesium is -2.37V, which is lower than Fe, Cu, Ni, Co and other metal elements and impurities contained in the alloy, making the alloy easy to form galvanic corrosion with heterogeneous metals. Under the action of potential difference, electrochemical reaction occurs, which makes the alloy easy to corrode and hinders the development of magnesium alloy[2]. Therefore, the study of magnesium alloy and the improvement of its corrosion resistance by alloying method have a positive role in promoting the application of magnesium alloy. The effect of trace calcium on the corrosion resistance of ZA124 magnesium alloy was discussed.

2. Test materials and methods
The test material was ZA124 magnesium alloy. The addition amount of Ca (mass fraction, %) was 0, 0.3, 0.6, 0.9, respectively. The chemical composition of ZA124-xCa alloy was shown in Table 1. The alloy material was smelted in a well type resistance furnace and then was processed into alloy samples.

The microstructure of the alloy was observed by XJ-16A optical microscope. The samples were electrochemically measured by AUTO TEST PS-168A three-electrode system with scanning speed of 2 mV/s. The alloy sample size of immersion weightlessness corrosion test was a cylinder (Ф20mmx15mm). The solution used in the corrosion test was 3.5% NaCl, the corrosion temperature was 25°C, and the corrosion products were removed by a mixture of 20% chromic acid and 1% silver nitrate. Soaking weight loss corrosion rate:

$$\nu = \frac{m_2 - m_1}{S \cdot t}$$
Where \(m_2\) was the mass of the alloy sample before immersion and weightlessness corrosion (g); \(m_1\) was the mass of corrosion products removed after the alloy sample was immersed in weightlessness corrosion(g); \(S\) was the contact area between the alloy sample and the corrosive medium solution during the corrosion process(m²); \(t\) was the corrosion time of the alloy sample in the corrosion solution(h).

Table 1 Chemical composition of ZA124- xCa alloys (wt%)

| Alloy      | Zn | Al | Ca | Be | Mn | Mg |
|------------|----|----|----|----|----|----|
| ZA124      | 12 | 4  | 0  | 0.01 | 0.25 | Bal. |
| ZA124-0.3Ca | 12 | 4  | 0.3 | 0.01 | 0.25 | Bal. |
| ZA124-0.6Ca | 12 | 4  | 0.6 | 0.01 | 0.25 | Bal. |
| ZA124-0.9Ca | 12 | 4  | 0.9 | 0.01 | 0.25 | Bal. |

3. Results and discussion

3.1 Metallographic analysis

Figure 1 shows the metallographic structure of ZA124 alloy with calcium content of 0, 0.3%, 0.6% and 0.9%, respectively. It was known that the alloy was mainly composed of \(\alpha\)-Mg matrix and the second phase with network distribution. According to the Mg-Zn-Al ternary phase diagram and Yang Mingbo's research results[3], ZA124 magnesium alloy was composed of \(\alpha\)-Mg matrix, \(\text{Mg}_{32}(\text{Al,Zn})_{49}\) and \(\text{Al}_2\text{Mg}_5\text{Zn}_2\).

![Figure 1. Metallographic microstructure of ZA124-xCa alloy](image)

As can be seen from Figure 1, ZA124 alloy without Ca was composed of matrix, reticular phase and small block phase. With the addition of 0.3% Ca, no new phase appeared in the alloy, but its microstructure was refined and the reticular phase became fine and discontinuous or strip. After adding 0.6% Ca, part of the network phase of the alloy became continuous. When the calcium content was 0.9%, the microstructure of the alloy was obviously coarsened and the continuous reticular phase increased. With the increase of calcium content, no new phase was formed in the alloy, but the microstructure and morphology of the alloy changed, first refined and then coarsened. Microamount of calcium alloying can refine the casting structure and improve the properties of magnesium alloys [4,5].

3.2 Effect of trace Ca on corrosion resistance of ZA124 magnesium alloy

3.2.1 Immersion weightlessness corrosion

The corrosion rate curves of ZA124-xCa (x=0, 0.3, 0.6, 0.9) alloy immersed in 3.5%NaCl solution for 120h were shown in Figure 2. The corrosion rate of ZA124-xCa (x = 0, 0.3, 0.6, 0.9) alloy was different after 24 hours of immersion weight loss corrosion. The corrosion rate of ZA124 alloy was higher than that of the alloy with Ca addition. The corrosion rate of ZA124 alloy was 1.7, 1.4 and 1.2 times of that of ZA124-xCa (x = 0.3, 0.6, 0.9), respectively. The addition of calcium can inhibit the corrosion of chloride ion on the alloy.

The corrosion rate of ZA124-xCa (x=0, 0.3, 0.6, 0.9) alloys increased with the increase of corrosion time in the process of immersion weightlessness corrosion for 24h to 72h. The corrosion rate
of alloy without calcium element was significantly higher than that of ZA124-xCa (x=0.3, 0.6, 0.9). Corrosion rates of ZA124-xCa (x=0.3, 0.6, 0.9) alloys were in good agreement with the curve of corrosion time. The corrosion rate increased slowly with the increase of corrosion time. The corrosion rate of ZA124 alloy with 0.3Ca alloy was the smallest in this process. The corrosion rate of ZA124 alloy with 0.6Ca was the middle, and that of 0.9Ca alloy was the largest. The curve of ZA124 alloy without Ca fluctuated greatly, and the corrosion rate increased rapidly with the increase of corrosion time. In the process of immersion weightlessness corrosion for 96h to 120h, the static weightlessness corrosion rates of the four alloys increased with the increase of the immersion time of the alloy in 3.5% NaCl corrosive medium. The static weightlessness corrosion rate of ZA124 without calcium was much higher than that of ZA124-xCa (x=0.3, 0.6, 0.9) alloys.

Figure 2. Corrosion rates of ZA124-xCa alloy immersed in 3.5% NaCl solution

When the static weightlessness corrosion test was conducted for 120h, the static weightlessness corrosion rates of ZA124-xCa (x=0.3, 0.6, 0.9) alloys reached the maximum value of this test, and the static weightlessness corrosion rate of ZA124 alloy without Ca was 2.3, 2.0, and 1.7 times higher than that of ZA124-xCa (x=0.3, 0.6, 0.9) alloy, respectively. A small amount of calcium can improve the corrosion resistance of magnesium alloy [5]. The addition of trace calcium refined the microstructure of ZA124 alloy, and made the microstructure of ZA124 alloy distribute uniformly, which was beneficial to improve the corrosion resistance of ZA124 alloy.

The static weight loss corrosion rates of ZA124-xCa (x=0.3, 0.6, 0.9) alloys were lower than those of ZA124 alloys without Ca addition during 120h of immersion weight loss corrosion. The corrosion resistance of ZA124 alloys was enhanced by adding Ca element. In this experiment, ZA124-0.3Ca alloy had the lowest corrosion rate and the best corrosion resistance.

3.2.2 Electrochemical corrosion analysis

The less Gibbs free energy the metal has in the process of forming ions, the more easily it will be corroded. In the Mg-Zn-Al alloy system with calcium addition, ΔG_{Ca}^{2+}<ΔG_{Zn}^{2+}<ΔG_{Al}^{3+}<ΔG_{Mg}^{2+}<0, calcium can protect the magnesium matrix [6]. The polarization curves of ZA124-xCa alloy were shown in Figure 3. As shown in Figure 3, the polarization curves of the four alloys had no passivation zone, and the alloys showed active dissolution. The addition of Ca was beneficial to increase the corrosion potential of ZA124 alloy, and the addition of Ca was helpful to improve the corrosion resistance of ZA124 alloy from the perspective of thermodynamics. The polarization curves of ZA124-xCa (x=0, 0.3, 0.6, 0.9) alloys in 3.5% NaCl solution were fitted by Tafel method. The self-corrosion potential of ZA124-xCa (x=0, 0.3, 0.6, 0.9) alloys were -1636 mV, -1131 mV, -1585 mV, -1628 mV, respectively. The corrosion current densities of ZA124-xCa (x=0, 0.3, 0.6, 0.9) alloys were 0.0161mA·cm^{-2}, 0.0034mA·cm^{-2}, 0.0061mA·cm^{-2}, 0.0063mA·cm^{-2}, respectively. The addition of calcium changed the anodic polarization curve and cathodic polarization curve of ZA124 alloy, and the
The self-corrosion potential and self-corrosion current density of ZA124 alloy were changed. The self-corrosion potential of ZA124-xCa (x=0.3, 0.6, 0.9) alloy were changed with the increase of calcium content, and were larger than that of ZA124 alloy without calcium addition. At the same time, the self-corrosion current density of ZA124-xCa (x=0.3, 0.6, 0.9) alloys decreased first and then increased. The corrosion current density of ZA124-xCa (x=0.3, 0.6, 0.9) alloys with 0.9Ca addition was the largest among the three alloys. The corrosion resistance of the alloy increased with the decrease of corrosion current density[7].The corrosion current density of ZA124 alloy was 4.7, 2.6 and 2.5 times higher than that of ZA124-xCa (x=0.3, 0.6, 0.9) alloy, respectively. It indicated that adding Ca element would significantly improve the corrosion resistance of ZA124 alloy. In this experiment, ZA124-0.3Ca alloy showed the best corrosion resistance. This was consistent with the conclusion of immersion weightlessness corrosion.

4. Conclusion

ZA124-xCa(x=0, 0.3, 0.6, 0.9) alloy was composed of α-Mg matrix, Mg_{32}(Al,Zn)_{49} and Al_{2}Mg_{5}Zn_{2}. The microstructure of the alloys with appropriate amount of Ca element was refined, the network transformation was fine and intermittent or strip-like. In the process of immersion weightlessness corrosion for 120h, the static weightlessness corrosion rates of ZA124-xCa (x=0.3, 0.6, 0.9) alloy were all lower than that of ZA124 alloy without adding calcium. The addition of trace calcium refined the microstructure of ZA124 alloy and made the microstructure of ZA124 alloy distribute evenly, which was conducive to improving the corrosion resistance of ZA124 alloy. ZA124-0.3Ca alloy had the lowest corrosion rate and the best corrosion resistance. In the electrochemical corrosion experiment, the addition of Ca element was beneficial to improve the corrosion potential of ZA124 alloy. The corrosion current density of ZA124 alloy was 4.7, 2.6 and 2.5 times of that of ZA124-xCa (x=0.3, 0.6, 0.9) alloy. ZA124-0.3Ca alloy had the best corrosion resistance. The results showed that adding Ca element would improve the corrosion resistance of ZA124 alloy.

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