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Effects of Ti and Zr elements addition on the microstructure and corrosion resistance of Zn-2.5Al-2Mg alloy

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Keywords: Zn–Al–Mg, corrosion resistance, micro-alloying

Abstract

In this article, the effects of Ti and Zr elements addition on the microstructure and corrosion resistance of Zn-2.5Al-2Mg alloy were studied. The microstructure, micro hardness, corrosion resistance of Zn-2.5Al-2Mg alloy were investigated by x-ray diffraction (XRD), Scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), Rockwell hardness tester and Electrochemical workstation, respectively. The result shows that the solidified structure of Zn-2.5Al-2Mg alloys was refined by Al₃Ti, Al₃Zr and Al₃(Ti, Zr) which act as a heterogeneous nucleation site. Moreover, the Rockwell hardness of Zn-2.5Al-2Mg alloys with the addition of Zr was significantly increased. The hardness of this alloy with the same amount of Zr and Ti addition is lower than that of the alloy with Zr addition alone, but obviously higher than that of the alloy with Ti alone. The corrosion resistance of the Zn-2.5Al-2Mg alloys with the same amount of Zr and Ti addition was improved significantly.

1. Introduction

Steel with excellent properties, such as high strength and hardness, wear resistance and easy processing, is one of the most widely used metallic materials in the world. Nevertheless, steel which was affected by various environments was easily corroded and invalid in practical situation. Hot-dip galvanizing is the most common way for steel anticorrosion, by forming a zinc layer on the surface of steel. The addition of Al element can improve the corrosion resistance of Zn-based coating, and several Zn–Al alloy coating systems have been developed, such as Galfan (Zn-5Al–Re) and Galvalume (Zn-55Al-1.6Si) [1, 2]. Recent years, the microstructure and corrosion resistance of Zn–Al–Mg alloy coatings have been widely reported [3–7]. And the hot-dip galvanized coatings, such as ZAM (Zn-6Al-3Mg), Super Dyma (Zn-11Al-3Mg-0.2Si) and PosMAC (Zn-2.5Al-3Mg) are extensively adopted for building industry, home appliance and automotive applications [8–12].

Solidification structure of alloy is the most significant for the performance and the surface appearance of the final products. A large number of scientific literature focused on the effect of alloying elements (Mg, Ti, Zr, Sb, Re, etc) on the microstructure and corrosion resistance of zinc-based coating [13–19]. It is believed that the corrosion and mechanical properties was strongly affected by the microstructure of zinc alloy coatings. It has been reported that the grain size in cast Al alloys with Ti and Zr addition was refined by the nucleation of Al₃Ti and Al₃Zr [20, 21]. Moreover, the Ti addition evidently refined the dendrite structure of the primary Al phase [22]. The addition of Ti can form a compact oxide film on the alloy surface, which has a good self-repairing ability and can prevent corrosion well [23–27]. Liu et al [28] studied the effect of Ti addition on microstructure and corrosion property of Zn-5Al alloy. The results showed that the addition of Ti refined the microstructure and improved the corrosion resistance of the alloy. Zhou et al [29] investigated the effect of Zr content on microstructure and corrosion resistance of hot-dip galvanized Zn-0.1%Ni-Zr alloy coating. The results showed that the addition of Zr significantly improved the corrosion resistance of Zn-0.1%Ni alloy coating. Li et al [30] studied the effect of Ti on solidification microstructure of Super Dyma alloy. The results showed that the Al-rich
dendrites were obviously refined, the size of the MgZn2 phase was greatly reduced and the Zn/Al/MgZn2 ternary eutectic structure was significantly refined.

Additionally, Ti and Zr elements are the important alloying elements in Al-based alloys and the addition of Ti or Zr elements alone in Al-based alloys has been widely studied [31–33]. It is generally believed that the Ti and Zr addition can effectively improve the corrosion resistance and the mechanical properties of Al-based alloys. However, there are few studies on the effect of the same content of Ti and Zr additions on the electrochemical properties of Zn–Al–Mg alloy.

With the increasing service requirements, traditional hot-dip alloys cannot meet people’s needs. In recent years, a variety of multi-elemental zinc-based coatings have been developed, and the Zn–Al–Mg alloy coating is the most concerned one. In this work, the effects of Ti and Zr elements on the microstructures and corrosion resistance of Zn–2.5Al–2Mg alloy were studied. The addition of Ti and Zr elements individually or in equal quantities together has been studied in detail.

2. Experiment

Model alloys Zn–2.5Al–2Mg–xTi–yZr were prepared with zinc (99.99%), aluminum (99.5%), magnesium (99.99%), and Al–Ti, Al–Zr master alloys. All the solutions were prepared with analytical pure regents and the deionized water. Zn–2.5Al–2Mg–xTi–yZr alloys were melted at 720 °C and kept at the temperature for 3 h to dissolve and homogenize in an electric resistance furnace under the argon atmosphere. Afterward, the melt was cooled to 550 °C and kept at the temperature for 2 h. Subsequently, the melt was cast into an ingot under atmospheric conditions. The chemical compositions of the cast alloys were detected by x-ray fluorescence spectrometer (XRF, Bruker Tiger S8) and corresponding results were presented in Table 1.

The structure and composition of the prepared alloys were investigated by x-ray diffraction (XRD, D8-advanY), scanning electron microscope (SEM, FEG250) and energy dispersive spectroscopy (EDS), respectively. The Rockwell hardness of the tested samples were measured by Rockwell hardness tester (HBRV-187.5).

All the electrochemical tests were using an IM6d Zahner-Elektrik workstations in 5 wt% NaCl solution at room temperature, taking platinum foil as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and Zn–2.5Al–2Mg–xTi–yZr alloy with an exposed area of 1 cm2 as a working electrode. The electrochemical measurements performed after the open circuit potential (OCP) was steady. Impedance spectra were obtained in the frequency range of $10^{-1}$ Hz – $10^5$ Hz and the signal amplitude was set to 10 mV. Moreover, the samples were polarized from $-3.5$ to 1.5 V versus SCE and the free corrosion potential at a rate of 10 mV s$^{-1}$.

3. Results and discussion

The XRD spectrum of Zn–2.5Al–2Mg alloy in figure 1(a) qualitatively indicated that the dominant phases were Zn, Al and MgZn2. The rest peaks were so weak that the existence of MgZn1 cannot be verified. In addition, it cannot satisfy the condition of phase quantitative analysis by XRD because the sample was as-casted and there was strong preferred orientation. The typical structures of Zn–2.5Al–2Mg alloy was shown in figure 1(b). The spherical and gray dendrites was Zn-rich grain, and the granular/lamellar region surrounding the dendrite was Zn/Al/MgZn2 ternary eutectic. In addition, there are a small amount of Zn/MgZn2 binary eutectic surrounding the Zn phase.
The SEM images of Zn-2.5Al-2Mg-xTi (x = 0.05, 0.1, 0.15) alloys are shown in figures 2(a)–(c). The microstructure of the cast alloys are extremely resembled. Although the total area of Zn-rich particles did not differ substantially, it was mostly composed of the Zn phase, Zn/Al/MgZn2 phases and the dark bulk-like Al3Ti phase distributed in the middle of the Zn grains. The EDS analysis of Zn-2.5Al-2Mg-0.1Ti alloy was shown in figure 3 and table 2. P1 with higher Al content is α-Al phase in the granular/lamellar region. The atomic ratio in

| Alloys designation | Nominal composition | Chemical composition (wt%) |
|--------------------|---------------------|---------------------------|
|                    |                     | Al | Mg | Ti | Zr | Zn |
| M                  | Zn-2.5Al-2Mg        | 2.54 | 1.96 | / | / | Bal. |
| M-0.05Ti           | Zn-2.5Al-2Mg-0.05Ti | 2.53 | 1.97 | 0.05 | / | Bal. |
| M-0.1Ti            | Zn-2.5Al-2Mg-0.1Ti  | 2.52 | 2.01 | 0.1 | / | Bal. |
| M-0.15Ti           | Zn-2.5Al-2Mg-0.15Ti | 2.53 | 1.98 | 0.15 | / | Bal. |
| M-0.05Zr           | Zn-2.5Al-2Mg-0.05Zr | 2.52 | 2.02 | / | 0.05 | Bal. |
| M-0.1Zr            | Zn-2.5Al-2Mg-0.1Zr  | 2.53 | 1.99 | / | 0.1 | Bal. |
| M-0.15Zr           | Zn-2.5Al-2Mg-0.15Zr | 2.52 | 2.01 | / | 0.15 | Bal. |
| M-0.025(TiZr)      | Zn-2.5Al-2Mg-0.025(TiZr) | 2.50 | 1.97 | 0.025 | 0.025 | Bal. |
| M-0.05(TiZr)       | Zn-2.5Al-2Mg-0.05(TiZr) | 2.49 | 1.98 | 0.05 | 0.05 | Bal. |
| M-0.075(TiZr)      | Zn-2.5Al-2Mg-0.075(TiZr) | 2.51 | 1.99 | 0.075 | 0.075 | Bal. |

The SEM images of Zn-2.5Al-2Mg-xTi (x = 0.05, 0.1, 0.15) alloys are shown in figures 2(a)–(c). The microstructure of the cast alloys are extremely resembled. Although the total area of Zn-rich particles did not differ substantially, it was mostly composed of the Zn phase, Zn/Al/MgZn2 phases and the dark bulk-like Al3Ti phase distributed in the middle of the Zn grains. The EDS analysis of Zn-2.5Al-2Mg-0.1Ti alloy was shown in figure 3 and table 2. P1 with higher Al content is α-Al phase in the granular/lamellar region. The atomic ratio in
the dark area (P2) is close to Al: Ti = 3: 1, which indicates that it is Al,Ti phase. P3 with lower Al content located at 4.27 at. % is Zn phase.

The structure of Zn–2.5Al–2Mg–yZr (y = 0.05, 0.1, 0.15) alloys can be identified in figures 4(a)–(c). Unlike the structure of Zn–Al–Mg alloy, the addition of Zr results in the appearance of Al,TiZr phase. Figure 5 presents the SEM image and EDS-mapping of Zn–2.5Al–2Mg–0.1Zr alloy. It is noted that the lamellar region mainly includes Zn, Al and Mg. And the bright dendrite/globular region is mainly Zn with a small amount of Al dissolved. The gray block area is mainly the precipitated phase formed by Al and Zr. Additionally, through the detailed EDS analysis as shown in figure 6 and table 3, it can be confirm that the bulk-like phase is a type of Al,TiZr phase (P1, P4) which exist as the enhanced phases in Zn–Al–Mg alloys. The comprehensive properties of the

| Point | Element | Zn | Al | Mg | Ti |
|-------|---------|----|----|----|----|
| 1     |         | 49.73 | 50.25 | /  | /  |
| 2     |         | 19.04 | 57.73 | /  | 23.23 |
| 3     |         | 95.73 | 4.27 | /  | /  |

Figure 4. The SEM images of Zn–2.5Al–2Mg–yZr (y = 0.05, 0.1, 0.15) alloys (a)–(c).

Figure 5. SEM image and EDS mapping of Zn–2.5Al–2Mg–0.1Zr alloy.
alloy could be improved by the dispersed Al₃Zr phase particles which have high density and strong pinning effect on dislocation slip and grain boundary movement.

The SEM images of Zn-2.5Al-2Mg-xTi-yZr (x = y = 0.025, 0.05, 0.75) alloys are shown in figures 7(a)–(c) and the EDS analysis of Zn-2.5Al-2Mg-0.025(TiZr) is shown in figure 8 and table 4. Primary dendrites of the Zn phase (P2) with 87 at% Zn content, Al₃(Ti, Zr) phase (P1) and ternary eutectics (P3) composed of particles MgZn₂, Zn–Al solid solution and Zn phase can be identified. It is considered that the Al₃Zr phase will precipitate preferentially with the same amount Ti and Zr addition, when the temperature is above the peritectic reaction temperature of Al–Ti [34]. And when Al₃Zr just precipitates and not aggregate, the Al₃(Ti, Zr) phase was formed.

Table 3. Corresponding EDS analysis of Zn-2.5Al-2Mg-0.15Zr.

| Point | Element  |
|-------|----------|
|       | Zn  | Al  | Mg  | Zr  |
| 1     | 18.54| 52.05| /   | 29.42|
| 2     | 84.85| 3.77 | 11.98| /   |
| 3     | 94.04| 5.96 | /   | /   |
| 4     | 11.04| 60.71| /   | 28.25|

Figure 6. The EDS analysis of Zn-2.5Al-2Mg-0.15Zr.

Figure 7. The SEM images of Zn-2.5Al-2Mg-xTi-yZr (x = y = 0.025, 0.05, 0.75) alloys (a)–(c).
due to Ti in the melt replaced part of Zr in Al₃Zr phase, which can be used as effective nucleation particle to make the grains fine and uniform.

Figure 9 shows the Rockwell hardness diagram of Zn-2.5Al-2Mg-xTi-yZr alloys. It can be evidently seen that the Rockwell hardness value of Zn-2.5Al-2Mg alloys were all increased by the addition of Ti and Zr elements.

| Point | Element | Zn   | Al   | Mg   | Ti  | Zr  |
|-------|---------|------|------|------|-----|-----|
| 1     |         | 24.88| 49.30| /    | 15.17| 10.65|
| 2     |         | 72.97| 8.73 | 18.30| /   |     |
| 3     |         | 83.69| 7.37 | 8.94 | /   |     |
| 4     |         | 43.22| 37.91| 2.38 | 8.83| 7.66|
With the addition of Ti, the hardness value of the Zn–2.5Al–2Mg–xTi (region I) increases first and decreases afterwards. When Zr is added, the hardness value of the Zn–2.5Al–2Mg–xZr (region II) significantly increased. When the content of the addition Zr reached to 0.15 wt%, the Rockwell hardness value of the alloy reached to 71.8 HRB. The hardness value of the Zn–2.5Al–2Mg–xTi–yZr alloys (region III) was higher than that of Ti added and slightly lower than that of Zr added. The reasons may be as follows: (1) The Al₃Zr precipitated phase, which is hard and brittle, can improve the hardness of Zn–Al–Mg alloy. When the Al bath temperature is too high, aggregation is easy to occur in the solidification process due to Zr element has higher melting point, larger atomic radius and poor wettability. And the hardness of the alloy because of a large number of substitutional solid solution caused serious lattice distortion is greatly improved. (2) The Ti has little effect on the hardness of the alloy because the Al₃Ti phase has smaller atomic size, better coherence with the matrix and smaller lattice distortion. (3) The hardness with the same amount Ti and Zr addition is not higher than that of the addition of Zr element, because adding Ti can reduce the lattice distortion caused by Zr added. Therefore, the same amount Ti and Zr addition can combine the advantages of Ti and Zr to achieve a perfect match between the microstructure and mechanical properties of Zn–2.5Al–2Mg alloy.
curves of Zn-2.5Al-2Mg-xTi-yZr are shown in alloys decreases and increases gradually, respectively. The polarization curves of Zn-2.5Al-2Mg-xZr alloys are corrosion potential in corrosion resistance, which was characterized by a significantly lower corrosion current density and more noble corrosion potential, as shown in figure 10. As seen in figure 10, all the curves show similar characteristics that the Nyquist plots consist of two complex capacitive loop and the corresponding Bode plots suggest two time constant in all case. The time constant at high frequency reveals the charge transfer impedance in the electric double layer, and the capacitive reactance loop in the low frequency region may characterize the resistance of surface conversion film of the alloy. The corresponding B-P diagrams in figures 10(a), (d), (g), the loop length of these semicircles was increased by the addition of Ti and Zr, indicating that the modification enhanced the corrosion resistance of Zn-2.5Al-2Mg alloy. Based on the observation of Bode impedance |Z| diagrams in figures 10(c), (f), (i), the curve of Zn-2.5Al-2Mg alloy moved upward for a certain distance, which also indicated that the corrosion resistance of Zn-2.5Al-2Mg alloy was improved with the addition of Ti and Zr. The charge transfer resistance of the alloy and the width of the capacitance ring at high frequencies were enhanced with the addition of Ti and Zr. The reason may be that the defects in the structure are eliminated and the structure of alloy is more uniform with the addition of Ti and Zr.

To further interpret the interfacial reaction that occurred under the above situation, one equivalent circuit (EC) is employed for the EIS data fitting, as shown in figure 11. Rs is the solution resistance; Rct is the charge transfer resistance; Rc is the resistance of corrosion product layer; Q is the constant phase angle element; n is the dispersion coefficient, and the dimensionless constant range is 0–1.

The fitted EIS results for studied alloys were summarized in table 5. As compared in table 5, the Rs of all the tests are lower than 10 Ω cm², which are much lower than Rct and Rc, indicating that all tests were in a stable environment. The equivalent circuit model did not change after adding the Ti and Zr, indicating that the corrosion behaviour of the Zn-2.5Al-2Mg alloy did not change at the initial stage of corrosion. The Rct of Zn-2.5Al-2Mg-xTi-yZr alloys were much better than Zn-2.5Al-2Mg alloy. Zn-2.5Al-2Mg-0.05Ti alloy has the max corrosion potential and corrosion current density of Zn-2.5Al-2Mg-xTi alloys decreased and increases gradually, respectively. The polarization curves of Zn-2.5Al-2Mg-xTi alloys decreases and increases gradually, respectively. The polarization curves of Zn-2.5Al-2Mg-xZr alloys are shown in figure 12. It can be seen that the addition of Zr, the corrosion potential of Zn-2.5Al-2Mg alloy increases first and then decreases, the corrosion current decreases first and then increases. The polarization curves of Zn-2.5Al-2Mg-xTi-yZr are shown in figure 12(c). The trend of composite addition of Ti and Zr is similar to that of Zr added.

| Sample    | Rs(Ω cm²) | Parameter | Rct(Ω cm²) | χ2   |
|-----------|-----------|-----------|------------|------|
| M         | 4.659     | 46.95     | 87.44      | 6.75E-4 |
| M-0.05Ti  | 5.509     | 4675      | 8070       | 2.45E-3 |
| M-0.1Ti   | 7.431     | 4818      | 5112       | 3.14E-3 |
| M-0.15Ti  | 6.533     | 763.7     | 1211       | 1.09E-2 |
| M-0.05Zr  | 5.34      | 336.6     | 638        | 4.15E-3 |
| M-0.1Zr   | 5.676     | 707.7     | 2308       | 7.80E-4 |
| M-0.15Zr  | 7.933     | 103.7     | 202.5      | 2.60E-4 |
| M-0.025(TiZr) | 7.235 | 1735      | 2098       | 2.80E-4 |
| M-0.05(TiZr) | 5.962 | 951.7     | 3049       | 1.19E-3 |
| M-0.075(TiZr) | 6.835 | 804.5     | 2353       | 9.87E-4 |
The $E_{\text{corr}}$ (corrosion potential), $I_{\text{corr}}$ (corrosion current density) and $\Delta E$ (passivation region) of the polarization curve can be obtained by Tafel extrapolation, and the detailed electrochemical parameters are summarized in table 6. As can be seen from table 6, $E_{\text{corr}}$ and $I_{\text{corr}}$ of Zn-2.5Al-2Mg alloy are $-1.46046827$ V and $0.00158584621$ A·cm$^{-2}$, respectively. The $E_{\text{corr}}$ of Zn-2.5Al-2Mg alloy after adding Ti and Zr increased slightly and $I_{\text{corr}}$ decreased obviously. Among them, $E_{\text{corr}}$ and $I_{\text{corr}}$ of Zn-2.5Al-2Mg-0.05Ti, Zn-2.5Al-2Mg-0.1Zr and Zn-2.5Al-2Mg-0.05 (TiZr) are $-1.38660268$ V, $0.000650273377$ A·cm$^{-2}$, $-1.07262278$ V and $0.17247669$ V and $-1.07262278$ V and $0.17247669$ V and $0.00158584621$ A·cm$^{-2}$, respectively. The $E_{\text{corr}}$ of Zn-2.5Al-2Mg alloy after adding Ti and Zr increased slightly and $I_{\text{corr}}$ decreased obviously. Among them, $E_{\text{corr}}$ and $I_{\text{corr}}$ of Zn-2.5Al-2Mg-0.05Ti, Zn-2.5Al-2Mg-0.1Zr and Zn-2.5Al-2Mg-0.05 (TiZr) are $-1.38660268$ V, $0.000650273377$ A·cm$^{-2}$, $-1.07262278$ V and $0.17247669$ V and $-1.07262278$ V and $0.17247669$ V and $0.00158584621$ A·cm$^{-2}$, respectively. The $E_{\text{corr}}$ of Zn-2.5Al-2Mg-0.05Ti, Zn-2.5Al-2Mg-0.1Zr and Zn-2.5Al-2Mg-0.05 (TiZr) alloys increased by $0.0739$ V, $0.05543$ V and $0.10517$ V respectively, $I_{\text{corr}}$ decreased by $58.96\%$, $54.24\%$ and $64.67\%$ respectively. Moreover, the $\Delta E$ of Zn-2.5Al-2Mg alloy with Ti and Zr addition is slightly wider. And the $\Delta E$ of Zn-2.5Al-2Mg-0.05Ti, Zn-2.5Al-2Mg-0.1Zr and Zn-2.5Al-2Mg-0.05 (TiZr) alloys increased by $0.01725$ V, $0.02176$ V and $0.02996$ V, respectively. It is showed that the corrosion resistance of the alloy can be improved significantly by addition of Ti and Zr elements.

The reasons why Ti and Zr elements can significantly improve the corrosion resistance of the alloy may be as follows: (1) Ti and Zr have higher corrosion potential and better corrosion resistance; (2) Ti and Zr will form a
passivation film during the corrosion process, which will increase the width of the passivation zone and increase the corrosion resistance of the alloy.

4. Conclusions

(1) The solidified structure of Zn-2.5Al-2Mg alloy is mainly included Zn-rich grain, and the granular/lamellar Zn/Al/MgZn2 ternary eutectic. The Al3Ti, Al3Zr and Al3(Ti, Zr) phases are used as nucleation substrates to refine the alloy structure.

(2) The Rockwell hardness of Zn-2.5Al-2Mg alloy was improved by adding Ti and Zr elements. Especially, the hardness is increased most obviously when Zr added. The hardness of the same amount of Ti and Zr addition is not higher than that of the addition of Zr, because adding Ti can reduce the lattice distortion caused by adding Zr.

(3) The corrosion resistance of the alloy can be improved by adding Ti and Zr. Comparing the corrosion resistance of Zn-2.5Al-2Mg-xTi-yZr alloys, it is found that the corrosion resistance of the same amount of Ti and Zr addition is better.

Acknowledgments

This work was supported by Shandong Key Research and Development Program (No. 2019GGX102008) and the National Natural Science Foundation of China (Nos. 51701081).

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