Corrosion Behavior of Zinc Flat Plate and Zinc Helix in the Salt Spray Tests

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The corrosion rates, corrosion products and the cross section morphology characteristics of zinc flat plate and zinc helix exposed to the neutral salt spray are investigated using weight loss test, XRD and SEM techniques. The results show that the relationship between the corrosion weight loss and the exposure time of the two kinds of zinc specimens are followed by the power exponential equation \( \Delta W = k \cdot t^n \), while the corrosion rate of the zinc helix is significantly higher than that of the zinc flat plate; both samples exhibit a general corrosion morphology and the same corrosion products of \( \text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O} \), \( \text{ZnO} \), and \( \text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 \).

Keywords: Salt spray test, Zinc flat plate, Zinc helix, Weight loss, Cross section

1. Introduction

Zinc and its alloy coating are widely applied in the field of metal protection, especially used for the protection of steel materials due to its good corrosion resistance and relatively low price [1-3]. In general, it is used as sacrificial anode in cathodic protection of the matrix metal materials against corrosion. As for its practical uses, it is extensively used in the form of zinc coating in the power transmission grid equipment, such as the protection of transmission tower, electric power fitting etc [4-6]. Most of the power transmission grid equipment is serviced in the atmospheric environment, and numerous outdoor and indoor investigations have been made on the corrosion of zinc flat plate under Cl- environment [7-11]. According to Bernard et al. [7], NaCl particles can deposited and dissolved in the thin electrolyte film of the zinc surface in the environment containing Cl-, which enhanced the conductivity of the thin electrolyte film, as well as leading to an accelerated corrosion process. The main corrosion product is zinc hydroxide chloride (Zn5(OH)8Cl2·H2O) with a poor soluble, while the research from Friel, L. Veleva et al.[8-9] showed that the zinc hydroxide chloride (Zn5(OH)8Cl2·H2O) can be easily washed away by the
rainwater, thus it possesses a poor protective ability due to its solvable in weak acid environment. Sun et al.[10] had made a two-year survey of atmospheric corrosion on zinc flat plate in Liaoning province of China, the relationship between the corrosion rate of zinc flat plate and the environmental factors in the rural and industrial atmosphere in Liaoning area was obtained by using the linear regression method. The results indicated that the weight loss of zinc increased with the increasing of exposure time, and increased significantly in the marine atmosphere. The main corrosion products are ZnCl₂·4Zn(OH)₂, and as well as a small amount of ZnSO₄, ZnO and carbon containing compounds. Wang [11] studied the corrosion rule of zinc under the conditions of continuous and intermittent salt spray, respectively. They proposed that the corrosion kinetics of zinc specimens are both accordance with the exponential equation \( \Delta W = k t^n \), the corrosion products are mainly Zn₅(OH)₈Cl₂ and followed by ZnO. Furthermore, the change of Cl⁻ concentration had a significant impact on the weight loss of zinc.

Currently, the standards of ISO 8565: 1992 and ISO 9226: 1992 have provided two types of standard specimens, one is the flat plate, and the other is the helix. Most researchers used the flat plate specimen to study the corrosion behavior of the metal materials, while the helix specimens are rarely used. The aim of this paper is to study the differences of the corrosion behavior of zinc flat plate and zinc helix by means of neutral salt spray tests. At the same time, the characterization was performed by weight loss, X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

2.1. Specimen Preparation and Weight Loss Test

The tested specimens are pure zinc flat plate and pure zinc helix. The chemical composition of the zinc sample is listed in Table 1. The zinc flat plate specimens are rectangular with dimensions of 50 mm × 75 mm, and with a thickness of 1 mm. All the specimens were polished down to 500 grit. As for the zinc helix specimens, the zinc wires with a diameter of 3 mm were cut into a length of 1000 mm, and then wound to a 90 mm length helix by a stick with a diameter of 24mm.
Table 1. The chemical composition of the zinc sample.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe</th>
<th>Cu</th>
<th>Pb</th>
<th>Sn</th>
<th>Ca</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.012</td>
<td>0.0005</td>
<td>0.040</td>
<td>0.0005</td>
<td>0.0005</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Prior to the tests, the specimens were cleaned with acetone and then dried by compressed air, stored in desiccators with silica gel desiccant for 24 hours. The initial weight of the specimens was weighted by using the analytical balance. Removal of the corrosion products referred to standard ISO 8407. The loose corrosion products were scraped off by a plastic sheet, and then the residual corrosion products were chemically removed by immersion in the solution (100 g CH3COONH4 in distilled water to make 1000 ml) for 2~5 minutes at 70℃. Then the specimens was washed with abundant distilled water, dried and stored in desiccators with silica gel desiccant for 24 hours, finally weighted. The weight losses in each group were measured using three parallel samples. Simultaneously, the unexposed zinc specimens were used to calibrate the corrosion of substrate corroded by the chemical solution.

2.2. Test Methods and Parameters

2.2.1. Salt Spray Test Method

The neutral salt spray test was conducted according to ISO standard 9227: 1990, using a salt spray test machine (SC/KWT 450, Weiss Germany). The zinc flat plate specimens were placed at an angle of 20° from the vertical, while the zinc helix specimens were hanged on a plastic rail. All the specimens were placed separately from each other, and the salt spray fog was able to settle smoothly. The salt spray fog has a chemical composition of 5 wt.% NaCl solution (pH between 6.5 and 7.2). The temperature in the salt spray test machine maintains at 35℃.

2.2.2. Characterization of the Corrosion Products

The corrosion products of the zinc flat plate and the zinc helix (for salt spray test of 50 days) were scraped off respectively. The XRD were employed to characterize the corrosion products. XRD tests were carried out with an X-ray diffract meter (D8Advance, Bruker Germany) with Cu Kα radiation with 2θ ranging from 10° to 90° at a scan rate of 2°/min at room temperature. In addition, several small pieces of zinc flat plate and zinc helix were cut out for cross section tests, respectively (for salt spray test of 7 days and 50 days). The cross section morphology was characterized using scanning electron microscopy (SU1500, Japan).
3. Results and Discussion

3.1. The Relationship between Weight Loss and Test Time

The corrosion rates, corrosion products and the cross section morphology characteristics of zinc flat plate and zinc helix exposed to the neutral salt spray are investigated using weight loss test, XRD and SEM techniques. The results show that the relationship between the corrosion weight loss and the exposure time of the two kinds of zinc specimens are followed by the power exponential equation $\Delta W = k \cdot t^n$, while the corrosion rate of the zinc helix is significantly higher than that of the zinc flat plate; both samples exhibit a general corrosion morphology and the same corrosion products of Zn5(OH)8Cl2·H2O, ZnO, and Zn5(CO3)2(OH)6.

According to the fitted results, the two kinds of curves followed equation as below: $\Delta W = k \cdot t^n$.

Table 2 lists the fitted data; whereas the k and n are constants, R2 represents the quality of nonlinear curve fitting. It is seen in Fig. 1 that the zinc helix exhibits a higher corrosion rate than that of zinc flat plate. Fuentes et al.[12] studied the long term corrosion behavior of zinc (13-16a), it is proposed that the corrosion rate of zinc samples in marine atmosphere follows the equation:

$$\Delta W = 16.7 \cdot t^{0.771} \quad (R^2 = 0.99002)$$

![Figure 1. Relationship between mass loss and test time of zinc flat plate and zinc helix.](image)

According to the following equations (1) ~ (3), and combined with data in Table 2,
\[ \Delta W = k t^n. \]  
\[ \Delta W_{\text{out}} = k_{\text{out}} t_{\text{out}}^{n_1} = \Delta W_{\text{in}} = k_{\text{in}} t_{\text{in}}^{n_2}. \]  
\[ \ln t_{\text{in}} = \frac{1}{n_2} \ln k_2 + \frac{n_1}{n_2} \ln t_{\text{out}}. \]  

For zinc flat plate:

\[ t_{\text{in}} = 1.3765 t_{\text{out}}^{1.3075}. \]  

For zinc helix:

\[ t_{\text{in}} = 0.8003 t_{\text{out}}^{1.1737}. \]  

Namely, if the zinc samples were exposed indoor for 7 days, this equals to the corrosion value of the zinc flat plate exposing for 3.5 year and of zinc open type spiral exposing for 6.3 year.

Table 2. Results of corrosion kinetics curves for zinc flat plate and zinc helix.

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>n</th>
<th>$\Delta W$</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc flat plate</td>
<td>12.835</td>
<td>0.82376</td>
<td>$\Delta W=12.835t^{0.82376}$</td>
<td>0.99158</td>
</tr>
<tr>
<td>Zinc helix</td>
<td>20.488</td>
<td>0.91773</td>
<td>$\Delta W=20.488t^{0.91773}$</td>
<td>0.98586</td>
</tr>
</tbody>
</table>

As for zinc flat plate specimens in exposure, the upward side and the downward side of zinc flat plate were set for comparison. As shown in Fig. 2, the upward side normally exhibits a uniform corrosion while it shows a local corrosion for the downward side. Legault et al[15]. had proposed that the corrosion rate of sky-ward side exhibits a greater value than that of ground-ward side. The curve of corrosion rate follows the linear relation for the sky-ward side, while it belongs to parabolic relation for the ground-ward side.

As for open zinc helix, the whole sample was subjected to the salt spray and exhibited a uniform corrosion due to its typical shape. This is the main reason leading to the higher corrosion rate for the zinc helix specimens (will be discussed detailed in Section 3.3). It is noted that the calculations of service life for zinc flat plate and zinc helix are different, and should be paid attention.
3.2. Analysis of Corrosion Products

Fig. 3 shows the XRD patterns of zinc corrosion products formed on zinc flat plate and zinc helix. According to the ICDD-JCPDS and Refs.16-17, the main corrosion products for both kinds of specimens were Zn5(OH)8Cl2·H2O, ZnO, and Zn5(CO3)2(OH). There have been many studies focusing on the zinc corrosion behavior in service environment containing Cl- [18-22]. Firstly, zinc reacts with oxygen in environmental system to yield a thin zinc oxide film, which possesses the slight protective ability against corrosive ions. In the presence of electrolyte, the zinc oxide transforms into zinc hydroxide and then further changes into other types of corrosion products, such as Zn(OH)Cl.

Boshkov et al.[23] pointed out that the reduction of oxygen increased the pH value in damage area of used zinc sample and accelerated the formation of Zn5(OH)8Cl2·H2O.

A NaCl solution used in the salt spray test maintain a pH value from 6.5 to 7.2 in 35°C, as such there is a few CO2 in solution and exists in the type of CO3 and HCO3, which favors the formation of Zn5(CO3)2(OH)6[17].
3.3. Cross Section Morphology

As can be seen in Figs. 4, zinc flat plate and zinc helix experience serious corrosion in salt spray tests. The corrosion rate obviously increased for both specimens with the extension of exposure. Analyzing from the cross section images, the rust of zinc flat plate was dense and smooths (Fig. 4(c)). There however exist many cracks in the rust, and the exhibits an inferior density compared with that of zinc helix (Fig. 4(d)).

According to Binaries et al.[24], due to the formation, dissolution, flaking of, spoiling and diffusion process of corrosive ions, index n in corrosion kinetics equation for zinc is greater than 0.5, and close to 1. For our studies, index n for zinc helix (n=0.91773) is greater than that of zinc flat plate (n=0.82376). This indicates that the rust of zinc helix exhibits a critical corrosion than zinc flat plate, which is also supported by the cross section images (Figs. 4c and 4d).

Carter et al.[25] proposed that the corrosion of sky-ward side is more serious than the ground-ward side, the corrosion products formed on the zinc surface densely and uniformly (Figs. 2(b), Fig. 4(a), Fig. 4(c)). While the zinc helix exhibits a local corrosion. As for the zinc helix in this study, the rust layer was uniform and loose, at the same time existed many cracks (Figs. 2(a), Fig. 4(b), Fig. 4(d)). It is easier for corrosive ions (Cl-) to penetrate into the rust of zinc helix compared with that of zinc flat plate. This leads to the acceleration of corrosion rate and weight loss for zinc helix.
4. Conclusions

In the environment of salt spray, the relationship between weight loss and the exposure time of the two kinds of zinc samples are followed by the power exponential equation $\Delta W = k t^n$. The corrosion rate of the zinc helix is significantly higher than the zinc flat plate.

In the environment of salt spray, the zinc flat plate and zinc helix show morphology of general corrosion. Both the samples present the same corrosion products of Zn₅(OH)₈Cl₂·H₂O, ZnO, and Zn₅(CO₃)₂(OH)₆, which gives the rust layer a weak protective ability.

Acknowledgement

The work was supported by the National Natural Science Funds of China (No. 51271110) and the Project of Science and Technology of State Grid (No. 52130414004x). This work was also supported by Science and Technology Commission of Shanghai Municipality. (No: 14DZ2261000)

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