The Effect of Temperature and Dissolved Oxygen Concentration on the Electrochemical Behavior of Al-Zn-In-based Anodes

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Abstract

The electrochemical behavior of three types of aluminium anode at different temperatures and dissolved oxygen concentrations was studied. Current efficiency tests were carried out. SEM and EDX were also conducted. The results suggest that when the temperature is much lower than room temperature, the dissolution morphologies of Al-Zn-In and Al-Zn-In-Cd anodes are non-uniform, and the Al-Zn-In-Mg-Ti anode exhibits uniform dissolution morphology. At low temperature, the dissolved oxygen concentration only affected the attack behavior of the Al-Zn-In and Al-Zn-In-Cd anodes but had little influence on the attack behavior of the Al-Zn-In-Mg-Ti anode.

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Keywords: Aluminium; Temperature; dissolved oxygen; SEM; Cathodic protection;

1. Introduction

In the new century, ocean research has become one of the major indices of measuring the development of science and technology in various nations. Currently, deep-see research has become focus of scientists in every country, such as those Europe and America and Japan. Considering the depth of water being targeted for research, ocean cathodic protection systems that require frequent replacement of anodes and maintenance are no longer practical. Longer-lasting cathodic protection systems are needed. It is

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important to investigate the corrosion behavior of materials in deep water [1]. Deep-sea environmental factors, such as dissolved oxygen, temperature, salinity, pH, water velocity and fouling, are different from those of the shallow sea [2-7], which can induce totally different corrosion behavior of marine structures. Therefore, it is important to investigate the corrosion behavior of sacrificial anodes in deep water. However, there are only a few studies concentrated on the corrosion behavior of anodes in deep water and on the effect of deep water environmental factors on the dissolution behavior of sacrificial anodes is still unclear.

Aluminium sacrificial anodes are widely used in the marine cathodic protection of steel structures due to their excellent merits such as low density, high electrochemical equivalent, stable performance and low cost. The purpose of this study was to investigate the electrochemical behavior of three types of aluminium anode at low temperature and different dissolved oxygen concentrations (similar to the condition of 600- and 1000-metre-deep sea environments), to determine the influence of low temperature and the concentration of dissolved oxygen on the anode dissolution behavior and to determine the attack behavior of different aluminium anodes in a simulated deep-sea environment. This study represents an exploration into new sacrificial anodes for deep-sea applications.

2. Experimental

The chemical compositions of the three aluminium anodes studied are shown in Table 1. All samples were cut from as-cast ingots into cylinders 48 mm in height and 16 mm in diameter for current capacity experiments. The samples were washed with acetone, dried, weighed at a 10^{-4}g accuracy using an electronic analytical balance and stored in a desiccator. Accelerated tests were carried out to determine the anode efficiency, the open-circuit potential (OCP) and the closed-circuit potential (CCP) versus time, according to the test methods used to determine the electrochemical properties of sacrificial anodes GB/T 17848-1999. All potentials were measured with respect to a saturated calomel reference electrode (SCE).

Table 1. The composition of the three aluminium sacrificial anodes (wt%)

<table>
<thead>
<tr>
<th>No.</th>
<th>Zn</th>
<th>In</th>
<th>Cd</th>
<th>Mg</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Zn-In</td>
<td>5</td>
<td>0.02</td>
<td>Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Zn-In-Cd</td>
<td>5</td>
<td>0.02</td>
<td>0.1</td>
<td>Bal.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Zn-In-Mg-Ti</td>
<td>5</td>
<td>0.02</td>
<td>1</td>
<td>0.5</td>
<td>Bal.</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Experimental conditions of the efficiency test

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature ( °C)</th>
<th>Dissolved oxygen (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Qingdao area seawater was used as the solution for all experiments. The concentration of dissolved oxygen was controlled by aerating N₂ and measuring with a dissolved oxygen detector. After efficiency testing, the micro-dissolution morphology was characterised using a XL-30 scanning electron microscope (SEM) equipped with energy dispersive analysis (EDX). To study the influence of temperature and
dissolved oxygen concentration on the electrochemical behaviour of the aluminium sacrificial anode, different experimental conditions were applied in the experiment, as shown in Table 2.

3. Results and discussion

3.1. Studies on seawater with 6 ppm (wt %) dissolved oxygen concentration

The open-circuit potential (OCP) and closed-circuit potential (CCP) of the three aluminium anodes are shown in Fig. 1. The OCP and CCP showed different sensitivity to temperature. The Al-Zn-In-Cd anode exhibited a fluctuation in its OCP and CCP at different experimental temperatures. The same behaviour was obtained for the Al-Zn-In anode. The CCP of the aluminium anode should range from -1.10 V to -1.05 V in a deep water environment to make sure steel structures are effectively protected. Based on Fig. 1, it can be concluded that the Al-Zn-In and Al-Zn-In-Cd anodes should not be used in low temperature environments because the fluctuation in potential cannot ensure the anode supplies enough current output. Compared with the Al-Zn-In and Al-Zn-In-Cd anode, the Al-Zn-In-Mg-Ti exhibited stable OCP and CCP at all experimental temperatures, which indicates that the Al-Zn-In-Mg-Ti anode can ensure the steel structures have sufficient cathodic protection at low temperatures.

![Fig. 1. Plot of the potential of the three aluminium sacrificial anodes at 6 ppm (wt %) dissolved oxygen vs. temperature after 4 days of experiment: open-circuit potential (OCP), closed-circuit potential (CCP) (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).](image1)

![Fig. 2. Plot of the efficiency of the three aluminium sacrificial anodes at 6 ppm (wt %) dissolved oxygen vs. temperature after 4 days of experiment (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).](image2)
Fig. 3. The dissolution morphologies of the three aluminium sacrificial anodes at 6 ppm (wt %) dissolved oxygen after 4 days of experiment (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).

The current efficiency results of the three types of aluminium anodes at different temperatures with 6 ppm (wt %) dissolved oxygen are shown in Fig. 2, and the dissolution morphologies are shown in Fig. 3. The dissolution morphology of the Al-Zn-In alloy, including local deep and large pits along with a mostly undissolved surface, was observed at low temperatures; the same dissolution morphology was observed in the Al-Zn-In-Cd anode. Among the three types of aluminium anodes, the Al-Zn-In-Mg-Ti anode showed very good performance at the three experimental temperatures and 6 ppm (wt %) dissolved oxygen. This anode always exhibited a high current efficiency, almost around 90 %, stable CCP at the experimental temperatures and uniform dissolution morphology.

The different dissolution morphology performance is a reflection of the different solidification structure. Micrographs of the solidification structures of the Al-Zn-In and Al-Zn-In-Mg-Ti anodes are shown in Fig. 4. Because the Cd content in the Al-Zn-In-Cd anode is small (only 0.1% Cd is added) and the Cd is not the grain refiner element, the structure of the Al-Zn-In-Cd anode is almost the same as that of the Al-Zn-In anode. Based on Fig. 4, compared with the Al-Zn-In anode, the crystal size of the Al-Zn-In-Mg-Ti anode is smaller and there are more defects on the Al-Zn-In-Mg-Ti anode surface. The different solidification structure is the result of the different composition of the anode. The Ti in the Al-Zn-In-Mg-Ti anode can act as a grain refiner. During the solidification process, low-content Ti can concentrate ahead of the advancing solidification front and form the compound TiAl₃[8]. The TiAl₃ particles are first suspended in the melt. When the matrix begins to solidify, these particles localise in front of the advancing solidification crystal, prevent the formation of large crystal grains and produce small crystal grains. Although the solubility of Mg in aluminium is relatively high (2% in 20°C), it can still form a small amount of Al₃Mg₂Zn₃, Mg₂Zn₃, and MgZn₂ phases during the solidification procedure, and these phases can form defects on the anode surface. Furthermore, the combustion of Mg can take place during the melt process, despite the fact that Mg is added in the formation of Al-Mg alloy. Then, Mg combustion can form cavities on the anode surface and increase the amount of anode surface defects. The small crystal size can reduce mechanical loss during anode dissolution and prevent the anode from forming large localised pits, and the defects on the anode surface can ensure the formation of sufficient initial activation pits; this property turns out to be very important when the anode is used at low temperatures. In a low-temperature environment, ionic activity decreases. The metal ions produced in the surface pits cannot diffuse to the outer solution very well. Then, the concentration of the metal ions in the pits increases, and the pH in the pits decreases. In this situation, the attack can easily occur on the grain boundary, and the grain particle can fall off the matrix alloy and induce mechanical loss (as the case of Al-Zn-In and Al-Zn-In-Cd anode). However, when there are a sufficient number of initial activation points on the anode surface and the anode crystal size is refined, the dissolution morphology can be
uniform. The sufficient number of initial activation points can allow the anode to maintain a large amount of initial pits, and the refined crystal size can prevent the initial pits from forming deep pits. Then, at low temperatures, the pits formed on the anode surface are present in large number and small sizes, and the metal ions produced in the pit can diffuse to the outside solution in time. Consequently, the concentration of the metal ions formed in the pits is low, the mechanical loss can be reduced and the dissolution morphology is uniform.

The activation mechanism of the Al-Zn-In alloy has been investigated for a long time [9-14], and the formation of an amalgam is a key factor. When the temperature is reduced, the energy of hydrolysis of Al$^{3+}$ is not sufficiently high to make In form an amalgam with Al, and the activation effect of In ions is suppressed. From the results of the experiments at different temperature and dissolved oxygen concentrations, it can be concluded that temperature is an important factor that influences the electrochemical properties of aluminium sacrificial anodes. Considering the components of the Al-Zn-In and Al-Zn-In-Cd anode, there is no crystal refiner element and the anode crystal size is relatively large; moreover, there are few surface initial activation points, as can be seen in Fig. 4. As mentioned above, when the temperature decreases, the activation behaviour of aluminium anodes with large crystal sizes and few initial activation points will be suppressed. At low temperature, the ionic activity is lower than at room temperature. In this situation, the cation concentration in the pits of the anode surface increases and cannot diffuse to the solution in time, which can induce a decrease in pH in the pits and cause the depth of the pits to increase. When the pH in the pits decreases, it is easy to induce local corrosion and cause large crystal grains to fall off from the matrix alloy. When the diffusion of the metal ions from the active area to the other alloy surface is blocked, the metal ions can form corrosion products that are adhered to the pits regions; these adhered corrosion product can act as a passive film and make the anode potential shift in the positive direction, and then the potential fluctuation and localised large pits can be observed at low temperature. However, when the number of activation points on the anode surface increases and the crystal grains are refined, the effect of low temperature on the dissolution behaviour becomes weak. Based on the figures illustrating the dissolution morphology of the Al-Zn-In-Mg-Ti anode, the electrochemical behaviour of this anode in a low temperature environment is excellent, which results from the addition of the refining element Ti and refining of the solidification structure. The same behaviour has been reported in Al-Zn-In-Si [15] anodes, for which the current capacity and potential are independent of low temperature in the range from -5°C to 25°C. When the anode exhibits refined crystal size and a large number of initial activation points, uniformly distributed small pits easily form on the anode surface, and the metal ions formed in these pits can easily diffuse to the other alloy surface. There are even crystal particles that fall from the matrix; because the crystal size is small, it will not induce
large mechanical loss and will prevent the formation of large localised pits. Consequently, to obtain an anode with satisfactory electrochemical performance at low temperature, the anode crystal grain should be refined, and the initial activation points should be present in large numbers.

3.2. Studies in seawater with a 0.6-ppm (wt %) dissolved oxygen concentration

The open-circuit potential (OCP) and closed-circuit potential (CCP) of the three types of aluminium anode at 0.6-ppm (wt %) dissolved oxygen concentration at low temperature (4°C, 8°C) are shown in Fig. 5. Compared with Fig. 2, the OCP and CCP changed at a low dissolved oxygen concentration (0.6 ppm (wt %)) compared with a higher dissolved oxygen concentration (6 ppm (wt %)). The OCP and CCP of the Al-Zn-In anode at a dissolved oxygen concentration of 0.6 ppm (wt %) shifted in the positive direction at 4°C and the negative direction at 8°C compared with anode at a dissolved oxygen concentration of 6 ppm (wt %). The OCP of the Al-Zn-In-Cd anode exhibited the opposite behaviour with respect to the Al-Zn-In anode. The CCP of the Al-Zn-In-Cd anode at a dissolved oxygen concentration of 0.6 ppm (wt %) shifted in the negative direction at 4°C, as compared with the anode at 6 ppm (wt %) dissolved oxygen. The OCP and CCP of the Al-Zn-In-Mg-Ti anode shifted slightly in the positive direction at both 4°C and 8°C at 0.6 ppm (wt %) dissolved oxygen compared with the anode at 6 ppm (wt %) dissolved oxygen. The OCP and CCP fluctuation of the three types of aluminium anode at 0.6 ppm (wt %) dissolved oxygen was not very pronounced. These results suggest that the dissolved oxygen concentration had little influence on the potential of all three aluminium sacrificial anodes, but the low dissolved oxygen concentration (0.6 ppm (wt %)) can make the potential of the Al-Zn-In and Al-Zn-In-Cd anode slightly more negative and make the Al-Zn-In-Mg-Ti anode potential slightly more positive than that of the anodes at a higher dissolved oxygen concentration (0.6 ppm (wt %)).

The current efficiencies and dissolution morphologies of the three aluminium anodes at 0.6 ppm (wt %) dissolved oxygen are presented in Fig. 6 and Fig. 7, respectively. When the dissolved oxygen was very small, the current efficiency of the Al-Zn-In-Mg-Ti anode ranged from 89 % to 90 % and was approximately the same as that at 6 ppm (wt %) dissolved oxygen. The dissolution morphology of the Al-Zn-In-Mg-Ti anode was uniform at 0.6 ppm (wt %) dissolved oxygen. The result indicates that this anode could exhibit excellent electrochemical performance at a low temperature and low dissolved oxygen concentration. However, the Al-Zn-In and Al-Zn-In-Cd anodes did not present a high and stable current efficiency at 0.6 ppm (wt %) dissolved oxygen, and the dissolution morphologies of these two types anode were non-uniform. At 0.6 ppm (wt %) dissolved oxygen, the dissolved area of the Al-Zn-In and Al-Zn-In-Cd anodes is larger than that at 6 ppm (wt %), and the probable reason is as follows: there are two main cathodic depolarisation elements (O₂ and H⁺). When the dissolved oxygen concentration is high, there is sufficient dissolved oxygen to react in the cathodic reaction. When the anode surface passive film dissolves and there are no activated ions to re-deposit on it, the dissolved oxygen can react with the matrix aluminium and form a passive film. Moreover, the reduction reaction of O₂ can produce OH⁻, and the OH⁻ can react with the metal ions and forms deposits in the pit regions; then, the deposits adhered to the pit regions block the diffusion of the ions, the pits corrode more deeply and localised pits are observed. However, when the dissolved oxygen concentration is lower, the amount of oxygen that can react in the cathodic reaction is small, and the main cathodic depolarisation reaction is the reduction of H⁺. In this case, when the anode surface passive film is broken, there will not be sufficient dissolved oxygen to form a passive film, and the fresh aluminium will be connected to the outer solution and the dissolved area will then increase. In light of the above results, the Al-Zn-In and Al-Zn-In-Cd anode cannot be used at low temperatures and low concentration of dissolved oxygen.
Fig. 5. Plot of open-circuit potential (OCP) and closed-circuit potential (CCP) of the three anode in 0.6 ppm (wt %) dissolved oxygen concentration environment vs. temperature after 4 days of experiment (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).

Fig. 6. Plot of the efficiency of the three aluminium sacrificial anodes in 0.6 ppm (wt %) dissolved oxygen concentration environment vs. temperature after 4 days of experiment (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).

Fig. 7. The dissolution morphologies of the three aluminium sacrificial anodes in 0.6 ppm (wt %) dissolved oxygen concentration environment after 4 days of experiment (A: Al-Zn-In, B: Al-Zn-In-Cd, C: Al-Zn-In-Mg-Ti).
4. Conclusions

Temperature can dramatically influence the dissolution behaviour of Al-Zn-In and Al-Zn-In-Cd anodes. With the decrease in temperature, the dissolution morphology of Al-Zn-In and Al-Zn-In-Cd anodes is non-uniform, and the dissolution morphology of Al-Zn-In-Mg-Ti anodes is uniform at room temperature and low temperature.

The concentration of dissolved oxygen can affect the dissolution behaviour of Al-Zn-In and Al-Zn-In-Cd anodes in low-temperature environments, but it has little effect on the dissolution behaviour of Al-Zn-In-Mg-Ti anodes.

Ti can refine the crystal structure of aluminium anodes and improve the dissolution morphology in low-temperature and low-dissolved-oxygen-concentration environments. Small amounts of Ti can prevent the formation of large crystal grains and reduce the mechanical loss of the anode. The finer the anode crystal grain is, the better the performance of the anode becomes.

References