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Effect of aluminium on the passivation of zinc–aluminium alloys in artificial seawater at 80 °C

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ABSTRACT

The effect of Al (0.15, 0.3 and 1.0 wt.%) on the passivation of Zn–Al alloys in artificial seawater at 80 °C is investigated by electrochemical measurements, scanning electron microscopy (SEM) and X-ray diffraction (XRD). It is found that the presence of Al in Zn–Al alloys can retard passivation. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements show that Al increases the current density but decreases the corrosion resistance of passive films, respectively. Mott-Schottky analysis reveals that Al increases the electrical conductivity and the capacitance of the films. Passivation of Zn–Al alloys occurs in artificial seawater when the immersion time is between 120 and 288 h, due to the presence of various Zn and Al protective compounds at the surfaces. Depassivation occurs when the immersion time is between 288 and 720 h, probably due to the decrease of solution pH and the Cl^- penetration mechanism.

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1. Introduction

Cathodic protection is usually applied at offshore platforms in some vessels by using sacrificial anode. The attachment of sacrificial anodes to vessels has been commonly practice for century and continues to be an important mean of corrosion protection [1] because the sacrificial anodes are relatively cheap, easy to install and exhibits high efficiency [1,2]. In contrast to the impressed current method, the anodes can be used without an external current source. Mostly vessels are made of carbon steel. Pure (~99.995 wt.%) or impure (~99.2 wt.%) Zn is used as a sacrificial anode for corrosion protection of carbon steel. During operation at a platform the solution temperature in a vessel is usually lower than 60 °C, and sometimes above 60 °C (up to ~80 °C) for few hours or few days. At this condition, Zn anode was passivated. The potential of passivated Zn is higher than that of carbon steel [3]. Consequently, the change of polarity in the corrosion cell occurs and the carbon steel vessel becomes an anode that is susceptible to corrosion.

It is not recommended to use Zn anodes at temperatures higher than 50–60 °C due to the passivation and mechanical fragmentation by intergranular decohesion [4,5]. Pure Zn does not suffer intergranular decohesion but passivates above those temperatures [5]. Zn passivation is the consequence of Zn corrosion products' formation on the surface. Depending on the nature of the environment, different types of Zn corrosion products can develop. In seawater, corrosion products exhibit the morphology of white rust which is a thick, crumbly and porous layer consisting of $Zn_5(CO_3)_2(OH)_6$ (zinc hydroxycarbonate), ZnO (zinc oxide) and voluminous β-$Zn(OH)_2$ (zinc hydroxide) [6]. For long exposure in a marine atmosphere, the corrosion products formed on Zn include $Zn_5(CO_3)_2(OH)_6$, $Zn_5(OH)_8Cl_2{\cdot}H_2O$ (zinc hydroxychloride) [7,8] and $NaZn_4Cl(OH)_6SO_4{\cdot}6H_2O$ (sodium zinc chlorohydroxosulfate) [8–10]. The presence of either sulfate or chloride ions, or a combination of the two, can accelerate the white rust formation and lead to the formation of $ZnSO_4$ (zinc sulfate), $Zn_4SO_4(OH)_6{\cdot}nH_2O$ (zinc hydroxysulfate) and $Zn_{12}(OH)_{15}(SO_4)_3Cl_3{\cdot}5H_2O$ (zinc hydroxychlorosulfate) [6,10–13]. The pH of the environment also has an effect on the formation and dissolution of the protective film on Zn. The dissolution rate is low within the pH range of 6–12.5 [6,14], but at pH below 6 and above 12.5 severe corrosion can occur.

A Zn anode is developed by alloying additions to avoid passivation, increase capacity, and improve dissolution morphology and mechanical properties [15,16]. The impurity in the anode can either deteriorate or improve the performance. The presence of Fe more than 14 ppm has a harmful effect on Zn because it forms insoluble compound ($FeZn_{13}$) which acts as a local cathode [17]. Al addition is beneficial because a less noble Al/Fe intermetallic compound is formed which reduces the effect of local corrosion [1]. Generally, Al improves the uniformity of dissolution and thereby decreases the risk of mechanical detachment of undissolved Zn anode [16]. It is claimed that the newly developed Zn–Al–Mg anodes will carry out satisfactorily at elevated temperatures [5]. Nevertheless, a pure Zn anode has now been widely employed in offshore and onshore industries despite the risk to passivation.

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To have a better understanding on the role of Al on passivation of Zn–Al alloys, the effect of Al on the passivation of Zn–Al alloys in artificial seawater at 80 °C is investigated in this work. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were used to study the passivation and corrosion resistance of pure Zn and Zn–Al alloys. An equivalent circuit model was proposed to characterize the Zn/film and film/solution electrochemical interfaces. The morphology and chemical composition of passive films formed on pure Zn and Zn–Al alloys were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

2. Experimental procedures

2.1. Materials and solution

Pure Zn (~99.995 wt.%) supplied by Padaeng Industry Public Company Limited and Zn-0.15, 0.3 and 1.0 wt.% Al were used in the study. The pure Zn and Zn–Al alloys were melted in graphite crucibles, using electrical furnace at 700 °C for 2 h under $ZnCl_2$ and NH_4Cl fluxes to prevent oxidation. The cast alloys were cooled down in air, then homogenized at 200 °C for 24 h. The chemical composition (wt.%) as shown in Table 1 was measured by spark optical emission spectroscopy (Spark-OES) and inductively coupled plasma (ICP). The Zn alloys were cut for a required size ($2 \times 1 \times 0.3$ cm) by electric discharge machining (EDM). All samples were ground with silicon carbide papers No. 80-2000, polished with 1 μm diamond paste, cleaned carefully with distilled water, acetone, and then dried in air. The samples were etched in 2% Nital for microstructural investigation.

The solution for electrochemical tests was artificial seawater according to ASTM D1141 [18] (NaCl 24.53 g/L; $MgCl_2 \cdot 6H_2O$ 11.11 g/L; Na_2SO_4 (anhydrous) 4.09 g/L; $CaCl_2$ (anhydrous) 1.16 g/L; KCl 0.70 g/L; $NaHCO_3$ 0.20 g/L and KBr 0.10 g/L (pH 8.2)). Before performing all the electrochemical tests, the samples were immersed in the tested solution (pH 8.2) at 80 °C (±2 °C) for 0, 24, 48, 72, 96, 120, 168, 216, 288, 408, 528 and 720 h. This was performed using a water bath (LWB-206A, model). After the end of immersion of each period, the solution pH was again recorded.

2.2. Electrochemical tests

All electrochemical tests using three-electrode system in an electrochemical cell were carried out after immersion in artificial seawater for a specified period. The tested samples with surface area of 2.9 cm^2 (half of total surface area) were working electrodes. Pt plate was a counter electrode and the saturated calomel electrode (SCE) was used as a reference electrode. All electrochemical measurements were conducted using Potentiostat/Galvanostat (PGSTAT 302N).

2.2.1. Potentiodynamic polarization

The potentiodynamic polarization curves of the samples (at each period of immersion as described in section 2.1) were recorded at the applied potentials range of -1.7 to 0.5 V (vs. SCE) with a scan rate of 1 mV s^{-1}.

2.2.2. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis

After immersion for a desired period, the sample potentials were swept from corrosion potentials (E_{corr}) up to desired potentials according to the potentiodynamic polarization curves and then kept at those desired potentials during the EIS experiments. This was right away followed by EIS (at 0, 48, 120, 528 and 720 h of immersions) and Mott-Schottky (at 168 and 720 h of immersions) measurements. Only at 288 h of immersion, EIS was performed after the desired potentials were maintained for 30 min. The impedance spectra were recorded to characterize the electrochemical interface in a frequency range between 100 kHz and 10 mHz with 5 mV amplitude AC perturbation signal. The equivalent circuit models were evaluated by NOVA 1.7 software for impedance data fitting. The Mott-Schottky plots were analyzed in the potentials range of -1.0 to -0.3 V (vs. SCE) with applied frequency of 1 kHz.

2.3. Surfaces characterization

The passive film morphology of the samples after anodic polarization from corrosion potentials up to desired potentials (at 48, 288 and 720 h of immersions) was examined using a scanning electron microscope (SEM, JEOL JSM-5800LV). The chemical composition of the films at the same conditions of SEM investigation was evaluated by X-ray diffractometer (XRD, Rigaku SA-HFM3) using Cu Kα radiation with an accelerating voltage of 40 kV and a filament current of 40 mA at the scan rate of 0.02° s^{-1}. The XRD patterns were analyzed by ICDD database.

The overall sequence of experiments is shown in Fig. 1. To check reproducibility, all electrochemical measurements were carried out at least twice. The ranges of standard deviations for potentiodynamic polarization, EIS and Mott-Schottky measurements are $4–7 \times 10^{-5}$, $5–7 \times 10^{-4}$ and $2–4 \times 10^{-3}$, respectively.

3. Results

3.1. Microstructure

The microstructures of pure Zn and Zn–1.0Al alloy at 0 h of immersion are shown in Fig. 2. The OM images reveal that the intermetallic compounds for both Zn alloys were not found. This is confirmed by XRD result as shown in Fig. 3. The XRD patterns of polished pure Zn and Zn–1.0Al alloy show the existence of Zn only for pure Zn, and contain minor constituent of Al for

Table 1
Chemical composition of different Zn alloys (wt.%) measured by Spark-OES and ICP.

Alloys	Zn	Al	Fe	Pb	Cu	Cd	Sn
Pure Zn	Bal	<0.0001 <0.0001[a]	0.0006	0.0015	0.0008	<0.0001	<0.0001
Zn-0.15Al	Bal	0.140 0.126[a]	<0.001	<0.002	<0.001	<0.0001	<0.0001
Zn-0.3Al	Bal	0.295 0.289[a]	<0.001	<0.002	<0.001	<0.0001	<0.0001
Zn–1.0Al	Bal	0.980 0.977[a]	<0.001	<0.002	<0.001	<0.0001	<0.0001

[a] Measured by ICP.

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