The effect of metallic oxide deposition on the electrochemical behaviour of Al-Zn-Mg-Sn alloy in natural tropical seawater

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Abstract. The potential of aluminium alloys as anode materials in cathodic protection system has been explored and a significant improvement has been achieved. However, for marine application, it is quite difficult to maintain continuous activation process due to passivation behavior of aluminum alloys. Therefore, to choose the best activation mechanism for aluminium alloy in marine environment, it has to be considered from various points such as alloy composition and surface treatment. This paper report the effect of metallic ruthenium oxide (RuO2) deposition on the surface of as-cast Al-Zn-Mg-Sn alloy and to study the effect of its presence on the electrochemical behavior using direct current (DC) electrochemical polarization and current capacity measurement. The morphology and topography of corroded surface were studied by the aid of scanning electron microscope (SEM) and confocal laser scanning microscope (CLSM) respectively. Results from this study showed that the presence of intermetallic compound (Mg2Sn) and also mixed metal oxide compound (Al2O3 and RuO2) on the alloy surface has been very useful in improving electrochemical reaction and charge transfer activities in chloride containing solution. This study also showed that RuO2 catalytic coating applied on the surface of Al-Zn-Mg-Sn alloy has slightly increased the corrosion current density compared to Al-Zn-Mg-Sn without RuO2. The corrosion morphology and topography of corroded surface of Al-Zn-Mg-Sn alloy deposited with RuO2 was found more uniform corrosion attack with the formation of porous and fibrous mud-like crack on outer layer. Based on surface morphology and 3D topographic studies, these features were believed to facilitate ionic species adsorption and diffusion through corrosion product layer at solution-alloy interface. Deposited RuO2 films also was found to increase of current efficiency by more than 10%.

1. Introduction
Cast aluminium was first highlighted in the public on year 1885 in Paris [1]. However, due to the technology limitation at that moment and also the unknown characteristic and potential of aluminium, industry has refused to further explore it capability. A few decade later, aluminium has vastly used in multidiscipline area and one of it was in the corrosion control by cathodic protection system. It all started when marine engineers in that time started to realize that stern drives and outboard motors
require a little more care than zinc anode can give[2]. This component was the most expensive and very important to all boat and ship. The application of aluminium sacrificial anodes for the cathodic protection of steel structures has been practiced since early 1960s and has become a popular choice nowadays due to its abundance and excellent electrochemical properties [3-5]. For example, aluminium alloy generally used in ports to protect structures (e.g., docks, pontoon, etc.) because of its higher theoretical efficiency and other merits, such as a low density, vast availability, reasonable cost and its capability in providing higher driving potential throughout service life [6-10]. Sacrificial anodes have a difficult task, since they have to protect what is already a very active aluminium assembly. Installing cheap or sub-standard anodes will undoubtedly increase corrosion risk and potentially very expensive corrosion problems mitigation cost [11].

Domination of pitting dissolution, surface passivation and unstable corrosion potential, were among problems that has been reported associated with aluminium sacrificial anode [12]. Previous researchers have reported that the presence of passive oxide layer on aluminium alloy can be modified by the addition of alloying element and also by applying catalytic coating [13-18]. Both surface activation methods were meant to generate surface modification such as micro-structural electronic defects that may lead to passive oxide film rupture. The alloying element and catalytic coating will disturb Al₂O₃ bonding strength by sit placing impurities in between [12]. The addition of alloying element such as Hg, Ga, In, Sn, Bi may weaken the oxide layer by ease of ion penetration from electrolyte through the defected oxide layer thus generating continuous localized corrosion [16,18]. In order to improve electrochemical activity of aluminum alloy, IrO₂ and RuO₂ has been extensively used as catalytic coating for chlor-alkali production and dimensionally stable anode due to it good catalytic activity [16,18,20]. In this study, the potential of RuO₂ as a surface activator in improving electrochemical properties of Al-Zn-Mg-Sn alloy in tropical seawater will further be explored.

2. Materials and Methods

2.1. Specimen preparation and alloy composition

Cast aluminium alloy was prepared in a graphite crucible under the protection of argon gas (inert atmosphere). Pure metals were melted in the crucible at the temperature of 850°C using Al bead (purity 99.90%) as primary component. Samples were made into rod shape using preheated mild steel mould. As for Al-Zn-Mg-Sn alloy fabrication, 1.5%wt Sn was added into aluminium melted solution when approaching 650°C to minimized Sn oxidation. In the same time, Argon gas flowed into the chamber surrounding was increased from 5 to 8 litres/minute. Sample was then cooled down at room temperature before proceeds to the next process. The as-cast aluminium was then cut by low speed cutter at speed of 250 rpm. Sample then polished by using 400, 600, 800, 1000 grades emery paper for the final surface preparation. Before dipped in RuCl₃ precursor solution, sample was first degreased and washed using acetone and distilled water. To obtain an aluminium alloy deposited with RuO₂, samples were then dipped in 1000 ppm RuCl₃ solution, dried and heated at 400°C for 30 minutes. Prepared aluminum alloy samples compositions were shown in Table 1.

2.2. Electrochemical test & corroded surface evaluation

Polarization test was conducted by using three-electrode cell GAMRY Instruments Reference 3000 potentiostat/galvanostat/ZRA controlled by GAMRY Framework V5.65 and using Echem Analyst software for data analysis. Tafel fit was used in determining the corrosion rate (µm/y) as well as the corrosion current density. Saturated calomel electrode (SCE) is used as the reference electrode.
Table 1. Aluminium alloy chemical composition analysed by wavelength dispersive x-ray fluorescent spectrometer (WDXRF)

| Composition (wt. %) | Zn | Mg | Sn | Fe | Pb | Al  |
|--------------------|----|----|----|----|----|-----|
| Pure Al            | -  | -  | -  | 0.035 | - | Bal. |
| Al-Zn-Mg-Sn (substrate) | 5.38 | 1.87 | 1.42 | 0.013 | 0.0007 | Bal. |
| Substrate deposited RuO₂ | 5.42 | 1.86 | 1.42 | 0.044 | 0.006 | Bal. |

(REE) and high density graphite as counter electrode (CE). Sample was cut from the as-cast cylindrical alloy and drilled. 5 mm thickness of sample then polished up to grit 1000 followed by ultrasonic cleaning and finally dried in warm flowing air prior to each experiment. Potentiostatic polarization test started from cathodic to anodic potential by the range of ±250 mV with scanning rate set at 0.5mA/sec. Specimen exposed area was 1 cm², embedded in specimen water tight Teflon holder from Princeton Applied Research Company. Corrosion current density, \( i_{corr} \) can be calculated from stern-Geary equation [21].

\[
\begin{align*}
  i_{corr} &= \frac{B}{R_p}, \\
  B &= \frac{b_a b_c}{2.303 (b_a + b_c)}, \\
\end{align*}
\]

Where \( B \) is so-called the “Stern-Geary constant”, \( b_a \) and \( b_c \) are the Tafel slopes for the anodic and cathodic reactions, respectively. The fitted value of \( R_p \) represents the overall resistance of the surface corrosion, but does not identify the passive or active corrosion areas even though the latter has a major contribution to the measured \( R_p \). Derived from Faraday’s law, the following equation is applied to calculate the corrosion rate (CR).

\[
CR (\mu m/y) = 3.27 \times i_{corr} \times E.W./d
\]  

Where E.W. is the equivalent weight of alloy (g) and \( d \) is the density of alloy in gm/cm³. By substituting Eq. (1) into Eq. (3) and setting the values of E.W. and \( d \), Eq. (4) is obtained.

\[
CR (\mu m/y) = \frac{304.2}{R_p}
\]

Where the units of polarization resistance was \( \Omega \) cm². Experiments will be held in tropical seawater solution at 27°C of pH 8.1. The solution was taken from Teluk Batik, Perak which was located at the west coast of peninsular Malaysia. Surface morphology of the samples after RuO₂ deposition and polarization test was observed by Scanning Electron Microscope (SEM) model Zeiss VP 1430 equipped with Inca Oxford energy dispersive x-ray (EDX). Confocal laser scanning microscope (CLSM) Model Zeiss LSM 5 Pascal will be used for surface topography analysis. Data and images reconstruction will be examined by LSM Zen software to extract the important information related to surface roughness parameters.

2.3. Current capacity and efficiency

Both anode (working electrode) and cathode (steel) specimens were polished to 1000 grit, washed and finally rinsed with acetone. Individual dimension for disc shape anode was 0.6 cm in thickness and 2.10 cm in diameter. A cathode of rectangular shape had a dimension of 0.8 x 4.1 x 16.0 cm. The separation or distance between anode and cathode was 10 cm and anode weight was recorded before the test started. Both anode and cathode were immersed in a lightproof perspex tank containing 40 liter
of filtered tropical seawater medium for about 72 hours. A current density was supplied to the anode at amount of 0.5 mA/cm² and charge transfer reading recorded at coulometer after 72 hours would be taken for anode capacity determination. Anode specimen was then washed with water and soft brushed and dried. For weight loss determination, anode specimen was immersed in ammonium hydroxide solution for several minutes, dried and then dipped in a mixture of 50 g/l chromic acid and 10 g/l argentum nitrate for 30 seconds. Sample was then washed with water, rinsed with acetone and dried to determine their weight loss. Anode capacity measurement were determined by ASTM G97 (2007) as below [22].

\[
\text{Current capacity} = \frac{\text{Ah}}{M_1 - M_2} \quad \text{Ah/kg} \tag{5}
\]

where

- \( \text{Ah} \) = recorded charge transfer (Ampere-hour).
- \( M_1 \) = sample weight before polarized (g).
- \( M_2 \) = sample weight after polarized (g).

While for the current efficiency measurement were determined by:

\[
\text{Current efficiency} = \frac{\text{Measured current capacity}}{\text{Theoretical current capacity}} \times 100\% \tag{6}
\]

where

\[
\text{Theoretical current capacity} = \frac{(96,480 \text{ C} / 3,600 \text{ S})}{\text{Sample equivalent weight}} \quad \text{Ah/kg} \tag{7}
\]

3. Results and Discussion

3.1. Physical evaluation

As cast Al-Zn-Mg-Sn alloy was cut, polish and prepared for physical surface characterisation by the aid of SEM. As-cast alloy showed a dendrite structure with the existence of bright irregular shape spot spread all over the alloy surface (Figure 1a). The bright spot was believed to be an intermetallic compound located at the grain boundary of aluminum matrix. EDX analysis has been carried out to determine chemical composition at two different locations marked as spot 1 and spot 2 in Figure 1b. EDAX spectra showed the presence of high intensity peaks for elements such Mg, and Sn from the bright spot area (Figure 1c), meanwhile Al, Zn and Mg peaks were detected from the dark spot area (Figure 1d). Based on the EDX analysis, the bright spot was believed to be an intermetallic compound known as Mg₂Sn. Based on XRD spectrum data in previous study, Mg₂Sn formation can be correlated with the low solid solubility characteristic of Sn in aluminum matrix [23]. When Sn is added more then it solid solubility, it has a tendency to react with Mg and rejected to interdendrite structure, forming a stable Mg₂Sn intermetallic compound or secondary phases. This compound also has been reported to play an important role in modifying the oxide layer and electrical properties of Al-Zn-Mg-Sn alloy [24]. The surface morphology of as-cast Al-Zn-Mg-Sn alloy deposited with 1000 ppm RuO₂ and heated at 400°C for 30 minutes were shown in Figure 2. SEM micrograph showed the alloy surface has changed with a distinctive surface layer morphology including cracked surface layer ranging from micro to macro-crack, that similar to dry mud-crack feature reported by Roger et al. [25]. High intensity elemental peaks arises from EDAX spectra (Figure 2c & 2d), showed the presence of mixture or bimodal oxide layer such as Al₂O₃ and RuO₂ on the specimen surface. This mixed
oxide particles were similar to the TiO$_2$/RuO$_2$ system in dimensionally stable anode (DSA) as reported by Shibli et al [17, 18].

Figure 1. SEM images for (a) Polished surface of Al-Zn-Mg-Sn alloy (b) Magnified area of interest (c) EDX spectra at spot 1 and (d) EDX spectra at spot 2

3.2. Electrochemical evaluation of deposited and undeposited alloy samples

3.2.1. Polarization test & current capacity measurement

All samples have been polarized in order to investigate the effect of surface chemistry on activation of pure aluminium, deposited and undeposited aluminium alloy corrosion in seawater. Figure 5 showed polarization curves obtained for the samples after being polarized in tropical seawater medium. In this scope of study, parameters from Tafel plot has been analysed and presented in Table 2. The curved line obtained as Figure 3 is the total current (the sum of the anodic and cathodic currents). The sharp point in the curve is due to the logarithmic scale and it is the point where the current changes from anodic to cathodic or vice versa. This intersection point has shows both the $i_{corr}$ and the $E_{corr}$ value. The key parameter is the $i_{corr}$ as it is directly proportional to the corrosion rate of the aluminium alloys. RuO$_2$ deposited sample showed an enhanced corrosion rate with 336 µm/year and pure Al with the smallest (0.55 µm/year).
Figure 2. SEM micrograph of Al-Zn-Mg-Sn alloy deposited with RuO$_2$ and EDX analysis at spot 1 and 2 (Fig. 2c= spot 1, Fig. 2d= spot 2).

The increasing of corrosion rate for deposited sample is believed contributed from the presence of metallic RuO$_2$ coating on Al-Zn-Mg-Sn alloy surface which has synergistic effect in mobilizing the ionic species or enhanced ion-electron movement and catalyzing the the electrochemical process. Higher corrosion current density indicates active dissolution process occurs in the system and usually dominated by uniform corrosion. The uniformity of corrosion attack morphology for Al-Zn-Mg-Sn has been reported by Isa et al. which found that Al-Zn-Mg-Sn alloy tend to form secondary phase or intermetallic particle known as Mg$_2$Sn [14]. The presence of Mg$_2$Sn particle the in alloy will generates defect to the oxide layer by forming a thin and weak oxides properties on the surface of the alloy. When expose to aggressive chloride solution, this weak spot will became more vulnerable to the chloride attack. This attack usually started at the outer passive layer on top of Mg$_2$Sn intermetallic particles [12].
Figure 3. Polarisation (Tafel) plots of pure aluminium, Al-Zn-Mg-Sn and deposited RuO$_2$ aluminium alloy in tropical seawater.

Table 2. Parameters from Tafel analysis based on polarization plot in Figure 3.

| Specimen                          | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $i_{corr}$ ($\mu A/cm^2$) | Corr. Rate ($\mu m/year$) | $E_{corr}$ (mV,SCE) |
|----------------------------------|--------------------|--------------------|---------------------------|---------------------------|---------------------|
| Pure Al                          | 215.1              | 241                | 0.014                     | 0.55                      | -980                |
| Al-Zn-Mg-Sn                      | 85.7               | 131.5              | 1.6                       | 101.9                     | -1130               |
| Al-Zn-Mg-Sn deposited RuO$_2$    | 31.1               | 125.5              | 227                       | 336                       | -1120               |

Figure 4a, c and e showed surface morphology of pure Al, bare and Al-Zn-Mg-Sn alloys deposited RuO$_2$ after polarization test in tropical seawater solution. At this stage, it can be observed that corrosion phenomena visible on all samples with the severity of corrosion attack patterns were different. On pure Al sample, corrosion is initiated and occurs but slow and may be not propagated, hence the appearance of corrosion product layer is seen intact. A dense adherent layer of the corrosion product formed on the surface can block or reduce the current flow ($I_{corr}$) by increasing the electronic and ionic resistance during the test. On Al-Zn-Mg-Sn sample corrosion attack is initiated at grain boundary and propagated leading to the appearance of much widespread generalized pattern on its surface. Morphological aspect of corroded surface showed that both Al-Zn-Mg-Sn alloy surface (4c& 4e) and was heavily disintegrated compare to pure aluminium sample (4a). Deposited RuO$_2$ aluminium alloy surface showed mud-crack surface morphology and porous surface layer compared to undeposited Al-Zn-Mg-Sn alloy this type of corrosion product layer normally can be correlated with aggressive corrosion attack on the alloy surface [26].
### 3.2.2 Current Capacity measurement

Tables 3 showed that current capacity and efficiency differs according to the chemical composition. Without the presence of alloying elements, pure aluminium gave a significant decrease in current capacity. It is clearly shown that both alloying elements and metallic oxide (RuO$_2$ deposited on the sample) play a very important role on the current efficiency. For example, sample pure aluminium give 1756 Ah/kg current capacity while sample Al-Zn-Mg-Sn alloy gave only 2201 Ah/kg. Highest current capacity recorded for Al-Zn-Mg-Sn deposited with 1000 ppm RuO$_2$ and it is believed that the increase in the efficiency (88.78%) for this sample is caused by the presence of alloying elements (Mg,
Sn) and metal oxide deposited on the surface which can attributed to synergistic activation and enhanced electrochemical activities at alloy-solution interface.

Table 3. Current capacity and efficiency in tropical seawater for 72 hours

| Specimen                   | Weight loss (g) | Current capacity Ah/kg | Efficiency (%) |
|----------------------------|-----------------|------------------------|----------------|
| Pure Al                    | 0.1522          | 1756                   | 59.00          |
| Al-Zn-Mg-Sn                | 0.1317          | 2201                   | 79.71          |
| Al-Zn-Mg-Sn deposited RuO₂ | 0.1048          | 2452                   | 88.78          |

3.3. Surface topography study

Surface roughness parameter such as average surface roughness (Ssa), surface skewness (Ssk) and surface kurtosis (Skₜ) were used to translate the specific topographical surface entity because single parameter was unable to describe the surface quality. Table 4 showed surface roughness parameters after polarization test and all the data were extracted from 3D scanning process and images in Figure-5. The average surface roughness for deposited RuO₂ sample slightly decrease after polariisation test and this result of lower Rₙa value after polariisation test is consistent with the nature uniform corrosion on the specimen surface. This decrease agrees with the widespread nature of corrosion attack that affects a large number of the scanning pixels in an image as shown in Figure 5. The negative value of surface skewness for undeposited Al-Zn-Mg-Sn sample (-0.07) representing predominance of valley structures on the alloy surface. The positive skewness value (0.102) for RuO₂ deposited Al-Zn-Mg-Sn alloy reflects unsymmetrical height distribution on the surface, with the presence of high peaks or filled valleys, and less deep scratch or a lack of peaks. From this observation, it was strongly believed that the presence of ruthenium oxide, RuO₂ in particles form on the alloy surface was believed to contribute to the better alloy dissolution process by creating a more uniform galvanic current distribution at the alloy-electrolyte interface and hence promoting non-localised and non-pitting corrosion attack. A positive Rₙsk value indicative of flat surface comprised of disproportioned number of peaks structure meanwhile surface with predominantly deep valleys, scratches or pores will tend to have a negative skewness value [27]. In this case, negative skewness values after polariisation test can be ascribed from the existence of deep pore structures, grain falling or dissolution process of an alloy when the sample was polarised in natural seawater. Kurtosis was a measure of peakness or sharpness of surface height distribution or sometimes qualifies the flatness of height distribution. Based on Table 4, kurtosis values in the range of 1.055 – 1.110 (Skₜ < 3) were recorded for samples after polarization test which indicate a corroded surface (Fig. 5c) with less peaks and valley structures. [28,29].

Table 4. Surface roughness parameter after polarization test

| Specimen                           | Ssa (μm) | Ssk (μm) | Skₜ (μm) |
|------------------------------------|----------|----------|----------|
| Pure Al                            | 98.031   | 0.062    | 1.110    |
| Al-Zn-Mg-Sn                        | 57.357   | -0.073   | 1.128    |
| Al-Zn-Mg-Sn deposited RuO₂         | 48.358   | 0.102    | 1.055    |
Figure 5. 3D CLSM constructed images of corroded surface after polarization test (a) Pure Al (b) Al-Zn-Mg-Sn alloy and (c) Al-Zn-Mg-Sn alloy deposited with RuO$_2$

4. Conclusion
In this study, both alloying addition (Mg, Sn) and metal oxide deposition (RuO$_2$) have proved their role in activating aluminium alloys in natural sea water. The presence of intermetallic compound (Mg$_2$Sn) in the Al-Zn-Mg alloy produced higher corrosion current density during polarisation process due to the cathodic nature of Sn as compared to Al matrix and thus initiated corrosion attack by uniform dissolution. As for the RuO$_2$ deposited Al-Zn-Mg-Sn alloy, it has successfully overcame the tendency of localised attack or pitting corrosion on the alloy surface by forming as catalytic activator layer for producing uniform and continuous dissolution process. The current capacity study showed that the presence of RuO$_2$ on the alloy surface can be very useful in reducing polarisation resistance of Al-Zn-Mg-Sn alloy at the early stage of immersion and maintaining ionic movement even after 72 hours of immersion. The RuO$_2$ metallic oxide has shown its usefulness by modifying the electrical properties of Al-Zn-Mg-Sn oxide layer by forming a porous and loose outer layer at the surface of the alloy. Surface topographic parameters for deposited Al-Zn-Mg-Sn alloy produce a lowest $S_{sa}$ values after polarisation process which was in a good agreement with current capacity of the alloy. This observation is a manifestation of better dissolution process occurs at the alloy Al-Zn-Mg-Sn deposited with RuO$_2$ in natural seawater.

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6. References

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