Effect of Copper and Silicon on Al-5\%Zn Alloy as a Candidate Low Voltage Sacrificial Anode

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Abstract. One common method used for corrosion protection is a sacrificial anode. Sacrificial anodes that usually employed in the marine environment are an aluminum alloy sacrificial anode, especially Al-Zn-In. However, the electronegativity of these alloys can cause corrosion overprotection and stress cracking (SCC) on a high-strength steel. Therefore, there is a development of the sacrificial anode aluminum low voltage to reduce the risk of overprotection. The addition of alloying elements such as Cu, Si, and Ge will minimize the possibility of overprotection. This study was conducted to analyze the effect of silicon and copper addition in Al-5Zn. The experiment started from casting the sacrificial anode aluminum uses electrical resistance furnace in a graphite crucible in 800°C. The results alloy was analyzed using Optical emission spectroscopy (OES), Differential scanning calorimetry, electrochemical impedance spectroscopy, and metallography. Aluminum alloy with the addition of a copper alloy is the most suitable and efficient to serve as a low-voltage sacrificial anode aluminum. Charge transfer resistivity of copper is smaller than silicon which indicates that the charge transfer between the metal and the electrolyte is easier to occur. Also, the current potential values in coupling with steel are also in the criteria range of low-voltage aluminum sacrificial anodes.

1. Introduction

Oil and gas offshore exploration faced corrosion problems that caused by aggressive environment because it deals directly with sea water. Therefore, the structures for offshore, subsea pipelines and constructions in direct contact with sea water should be protected. Several ways can be used to reduce the corrosion rate. One common method used is the method of cathodic protection. Sacrificial anode applied in the marine environment is al-Zn-In alloy. Aluminum is an excellent sacrificial anode which used in seawater environments. However, passivation behavior of aluminum after contacted with its environment resulting in lower the output current. Therefore, aluminum is usually combined with other elements are like tin, indium, mercury, as an activator.

The conventional aluminum alloy sacrificial anode is Al-Zn-In, but electronegativity of these alloys can cause overprotection steel.[1,2] Therefore, development of low voltage sacrificial anode aluminum to reduce the risk of overprotection is urgently required nowadays. Therefore, there is a development of the low voltage sacrificial anode aluminum to lessen the possibility of overprotection [3,4].

The most common alloying elements added to the aluminum sacrificial anode is Zn. Zn added ranged between 2.5% -5.75%. The addition of Zn element is intended to damage the passive layer of aluminum [5]. Formation of second phase particles will trigger de-passivation of aluminum or damage
to the passive layer of aluminum. It formed particles β-phase that caused damage to the passive layer of Al2O3 and increased efficiency of the sacrificial anode.

The addition of Cu will affect the strength and hardness of aluminum alloy. A Higher number of Cu, the corrosion resistance of aluminum will decrease. The main cause Cu may reduce the corrosion resistance of aluminum is not as solid-solution or a second phase formation, it resulting from a thin layer of Cu deposited on the surface of the alloy and formed a metallic copper cathode [6].

On the other hand, Silicon is a common alloy that is usually added to aluminum. Silicon is added to an alloy in aluminum sacrificial anodes are to reduce variation in corrosion and electrochemical properties[7]. The addition of silicon will improve the uniformity of the corrosion on the sacrificial anode because equiaxed fine grain and grain boundaries in which precipitates-silicon precipitates evenly distributed.

2. Methodology
Casting process of aluminum anode graphite crucible which under a heating temperature of 750°C and was held for 90 minutes. Remnants of impurities on the surface of the melt are removed before pouring process. Minimum purity each of element that used in this research was 99%. Each element is weighed to achieve a target composition of Al-5% Zn, Al-5Zn-(0.5-1%) Cu and Al-5Zn-(0.5-1%) Si. At least 2 Kg of sampling was achieved from each of casting process. The alloying process was done with holding the temperature at 750°C for 15 minutes. The stirring process was conducted for 20s to get a better homogenization. The casting product was characterized by several tests such as metallographic, optical emission spectroscopy and cyclic polarization test (Autolab PGSTAT302N). Cyclic polarization was done under 3.5%NaCl solution with scan rate 0.01mV/s, and potential range 1.0V to -1.0V.

3. Result

3.1 Optical Emission Spectroscopy
The chemical composition of each alloy was tested using Optical Emission Spectroscopy (OES). The result showed target composition has successfully achieved. Table 1 illustrates the result of OES testing.

| Sample       | Composition (wt.%) | |
|--------------|--------------------|---|
|              | Al | Zn | Cu | Fe | Si | Mn | Mg | In |
| Al-5Zn       | 94.9 | 4.90 | <0.001 | 0.041 | 0.115 | <0.001 | <0.0001 | <0.10 |
| Al-5Zn-0.5Cu | 93.4 | 5.16 | 0.571 | 0.058 | <0.800 | <0.0005 | 0.006 | <0.10 |
| Al-5Zn-1Cu   | 93.7 | 4.82 | 1.28 | 0.054 | 0.048 | <0.001 | 0.0005 | <0.01 |
| Al-5Zn-0.5Si | 94.8 | 4.55 | 0.561 | 0.034 | <0.001 | <0.001 | <0.0001 | <0.01 |
| Al-5Zn-1Si   | 93.6 | 4.85 | 1.27 | 0.070 | 0.0037 | 0.0051 | 0.0031 | <0.01 |

3.2 Metallographic
The metallographic test was conducted to compare the condition of metals before immersion and after immersion test. Based on the immersion test result, it can be seen that the material Al-5Zn-1Cu suffered severe corrosion than the Al-5Zn-1Si. Corrosion spread evenly at the entire alloy. It is because precipitate Cu at the secondary dendrite arm spacing region. Figure 1 showed corrosion of these alloy started from the dendrite secondaryarmspacing (SDAS) area. Precipitate in SDAS act as a cathode while area around the precipitates acted as anodic area.
Figure 1 Condition of Al-Zn-Cu alloy before immersion (A) and after immersion for five days (B)
At the Al-5Zn-1Si alloy, corrosion occurs around the intermetallic phase. However, corrosion attack is more benign compared with Al-5Zn-1Cu alloy. This condition showed intermetallic did not give sufficient effect compared with precipitate. Both of the alloys showed corrosion attack selectively at secondary dendrite arm spacing while the dendrite arm spacing are not attacked.

Figure 2 Condition of Al-Zn-Si alloy before immersion (A) and after immersion for five days (B)

3.3 Cyclic polarization
Based on cyclic polarization curve, materials with lower corrosion potential will be more susceptible to corrosion. Based on Figure 3 Al-5Zn alloy is the most vulnerable to corrosion due to the lowest potential than the other. On the other hand, Al-5Zn-1Cu has the highest potential than the other alloy candidate.
Figure 3 Cyclic polarization showed addition of copper would increase Eptumber
It can be seen quantitatively by Table 2. It can be seen that the pitting potential of Al-5Zn is equal to -0.94V vs. SCE and the most positive is the alloy Al-5Zn-1Cu -0.83 V vs. SCE. Even though Al-Zn1Cu increase the pitting potential of the alloy, it has the largest loop area. Higher loop area indicated corrosion would be propagated easier in the alloy due to longer time for oxide layer to re-passivated.

| Material Paduan         | Eb (V vs SCE) | Ep (V vs SCE) | Eb-Ep (V vs SCE) |
|-------------------------|---------------|---------------|------------------|
| Al                      | -0.76         | -0.83         | 0.07             |
| Al-5Zn                  | -0.94         | -1.14         | 0.2              |
| Al-5Zn-0.5Cu            | -0.89         | -1.03         | 0.14             |
| Al-5Zn-1Cu              | -0.83         | -0.99         | 0.16             |
| Al-5Zn-0.5Si            | -0.880        | -0.99         | 0.11             |
| Al-5Zn-1Si              | -0.872        | -0.97         | 0.10             |

4. Summary
Al-Zn-Cu alloy is the most suitable and efficient to be served as low-voltage sacrificial anode aluminium. It has higher corrosion rate and higher loop area. Precipitates Al-Zn-Cu give higher effect on corrosion than precipitate Al-Fe-Si

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