Study of Al-Zn-Cu-Sm Efficiency for Low-Voltage Sacrificial Anode Candidate

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Abstract. Sacrificial anode is one of the most effective methods for preventing corrosion in seawater environment. Aluminum (Al) anode works very well in seawater environment with high electrochemical capacity and high driving voltage. Commonly used aluminum alloy sacrificial anodes have the possibilities to trigger the occurrence of Stress Corrosion Cracking and Hydrogen Embrittlement due to overprotection on high-strength steel. The low voltage sacrificial anode was developed to overcome this problem. Electrochemical behavior of Al-5Zn-0.5Cu alloy with varied samarium (Sm) addition of 0.02 wt% and 0.1 wt% was investigated in this study. The commonly used Al-5Zn-0.02In alloy is also tested as a comparison. Anode efficiency test with weight loss method according to DNVGL-RP-B401 standard was conducted to determine the performance of Al-5Zn-0.5Cu-xSm alloy. The addition of 0.1 wt% Samarium shows the best anode performance with electrochemical capacity 2809.80 Ah/kg and 98% efficiency. Al-5Zn-0.5Cu-0.1Sm alloy is the most potential alloy to be developed as a low potential sacrificial anode to replace commonly used aluminum sacrificial anode with indium addition.

1. Introduction
Aluminum-based sacrificial anodes are the most common type of sacrificial anode used in seawater environments due to its high electrochemical capacity and high efficiency. The most commonly used sacrificial anode is Al-Zn-In. With the addition of indium to Al-Zn alloys, it will activate aluminum that will prevent the formation of a passive layer resulting increase of the efficiency of the sacrificial anode. This activation process will even more easily occur when in environments with high chloride ions such as in seawater environments[1]. However, the disadvantage of this sacrificial anode is that Al-Zn-In can initiate the occurrence of stress corrosion cracking and hydrogen embrittlement in high strength steels[2]. The low voltage sacrificial anode was developed to overcome the aforementioned problems. Low voltage sacrificial anode would have to supply a working potential around -0.8V vs SCE, because at this range of potentials the amount of hydrogen liberated is highly reduced and steel is still protected[2]. In its development, rare earth metals were used as additional alloying elements to modify the nature of the sacrificial anode. In previous studies, gallium[2], cadmium[2], and samarium[3] were used as alloying elements. The previous research suggests that samarium has promising results. This study aims to compare the efficiency of Al-Zn-In anodes with Al-Zn-Cu-Sm to develop low voltage sacrificial anode candidate. Electrochemical behavior of Al-5Zn-0.5Cu alloy
with varied samarium (Sm) addition of 0.02 wt% and 0.1 wt% compared to Al-5Zn-0.02In was investigated in this study.

Adding zinc (Zn) to aluminum-based anodes has the purpose of destabilizing the passive layer of the aluminum. The addition of zinc up to 5 wt% can optimize the working efficiency of aluminum anodes by increasing their electrochemical properties. The presence of undissolved $\beta$-phase in the aluminum matrix causes damage to the passive alumina layer on aluminum anodes which will increase the outgoing current, so that the efficiency of the sacrificial anode increases[4]. Although the addition of copper (Cu) in aluminum will increases strength, hardness, and machinability, it will reduce corrosion resistance of the aluminum, as well as increasing susceptibility to stress corrosion[5]. The addition of copper in Al-Zn alloy also affects the microstructure. Based on previous research, the initiation of pitting corrosion occurs due to the formation of Al$_3$Cu precipitates which tend to segregate at the grain boundary. Based on immersion testing, the area first attacked by pitting starts from the precipitate around the grain boundary. The lowest value of corrosion resistance is found at alloy Al-5Zn-1Cu[6].

Addition of samarium to aluminum alloy plays a role in changing the microstructure. The addition of the samarium element can change the morphology of $\alpha$-Al dendrites to be finer. Moreover, the addition also the phase rich in eutectic iron and silicon. Iron-rich phases will change morphology from irregular to thin morphologies. The volume fraction will also decrease[7]. The addition of the samarium also effected the silicon eutectic phase morphology. With the addition of 0.3 wt% samarium, the silicon eutectic becomes smoother and its sharp edges begin to disappear. The optimum morphology was achieved by adding 0.6 wt% samarium. However, excessive addition of samarium will cause the eutectic silicon to return to its original shape[8]. Pratesa et al. showed that the addition of samarium to Al-5Zn-0.5Cu alloy results in SmCu$_2$Al$_{11}$ precipitates after the solidification process[3].

2. Experimental method

2.1 Material Preparation

This research begins with casting the alloy from high purity aluminum, zinc, copper, and samarium ingot with 99.99% grade. The materials were cut into pieces, weighed and melted in graphite crucible in electric resistance furnace under atmospheric condition at 700°C. The mixture was gently stirred using a carbon bar to obtain a homogeneous mixture, as well as heat dissipation. The molten alloy was poured in a preheated cast iron die and allowed to cool in air. The process started with casting the master alloy of Al-5Zn-0.5Cu and Al-10Sm. The casting process continued with cutting master alloy then drying and weighing in accordance to obtain the alloying target. There are two types of alloy with samarium addition that will be made Al-5Zn-0.5Cu-0.02Sm and Al-5Zn-0.5Cu-0.15Sm. The next casting carried out is Al-5Zn-0.02In alloy which begins with cutting aluminum, zinc, and indium ingots according to their material balance and repeated the same casting procedure. Actual chemical composition of casted alloy was determined by Optical Emission Spectrometer and is given in Table 1.

2.2 Anode Current Efficiency

Anode efficiency testing has the purpose of determining the work efficiency of the sacrificial anode. The size of the samples was $\Phi$ 5 mm x 10 mm. Mild carbon steel and a silver/silver chloride were used as cathode and reference electrode, respectively. The minimum surface area ratio of test anode to cathode was 1:20. Anode and cathode were coupled and immersed together in aerated 10 liters of natural seawater. The temperature for this test must be maintained at 20°C ± 3°C. This test is carried out based on the DNVGL-RP-B401 standard[9]. The basic principle of this test is to discharge current with a certain predetermined current density for 96 hours of testing on the electrochemical cell circuit. Different current densities were employed ca. 1.5, 0.4, 4.0, 1.5 mA/cm$^2$. At the end of the test, the sample is cleaned with running water and soaked in a solution of 20 grams of CrO$_3$ and 30 ml of H$_3$PO$_4$ per liter of water for 10 minutes at 80°C. The sample is then washed with water followed by alcohol
and then dried. Final weight calculation is done after sample cleaning. The lost anode weight was calculated to determine the electrochemical capacity of the anode during the test. The electrochemical capacity has a unit of Ah / kg. This study was conducted at Department of Metallurgical and Materials Engineering Universitas Indonesia, Depok, Jawa Barat, Indonesia.

2.3 Metallographic Examination
Microstructure observation is carried out on samples after casting. This observation is carried out using an optical microscope. Each sample ground with #80 - #1500 silica paper and polished with 1µm diamond paste. In the sample preparation stage, no etching process done to prevent corrosion on the grain boundaries to be observed because precipitates tend to form at grain boundaries. This observation aims to determine the effect of the addition of alloying elements on grain shape, grain boundaries and precipitates formed. Microstructure examination also done after anode efficiency test using optical microscope. Samples that have been tested for efficiency are cut in the middle with 2.5 cm from the top with a cross section. Samples were prepared by grinding with silica paper up to 1200 grit and observed with optical microscopy. The whole samples are also observed by digital camera before cut. The purpose of this observation is to determine the form of corrosion that occurs on the surface of the sacrificial anode during efficiency testing.

3. Results and discussion

3.1 Chemical Composition
The chemical composition of the aluminum alloy sacrificial anodes after casting is obtained through Optical Emission Spectroscopy (OES) testing. Table 1 shows the results of chemical composition test for Al-5Zn-0.5Cu (Alloy A), Al-5Zn-0.5Cu-0.02Sm (Alloy B), Al-5Zn-0.5Cu-0.1Sm (Alloy C), and Al-5Zn-0.02In (Alloy D). The results of the composition testing in Table 1 show a deviation of chemical composition from the target. The desired zinc content in alloy A, B, and C samples is 5.0 wt%, however the actual composition has a deviation of 0.54, 0.07, and 0.04 respectively. The compositions of copper in alloy A, B, and C samples has a deviation of 0.06, 0.009, and 0.082 respectively of the desired targets of 0.5 wt%. The composition test results for alloy D sample have a deviation of 0.04 from the target of 5 wt% zinc and 0.0063 from the target of 0.02 wt% indium. The deviation of the main constituent elements of the alloy may be ignored because the deviation value is insignificant, so that the aluminum alloy from casting can be considered to have reached the target.

| Alloys | Zn Deviation | Cu Deviation | In Deviation | Al Deviation |
|--------|--------------|--------------|--------------|--------------|
| A      | 0.54         | 0.06         | < 0.01       | 93.8         | 0.20         |
| B      | 0.07         | 0.009        | < 0.01       | 94.3         | 0.18         |
| C      | 0.04         | 0.082        | < 0.01       | 94.1         | 0.30         |
| D      | 0.04         | < 0.001     | -            | 94.8         | 0.18         |

3.2 Electrochemical Performance
Based on the data obtained in Table 2, the electrochemical capacity obtained in Al-5Zn-0.5Cu alloy was 1852.83 Ah/kg with 65.08% efficiency. The electrochemical capacity and current efficiency increased with addition of samarium. This electrochemical capacity value indicates the ability of an alloy to work as a sacrificial anode in protecting the structure. The higher the value of the electrochemical capacity of an alloy, the better the protective ability[10]. Based on the results obtained on the two samples of the sacrificial anode with variations of samarium content, Al-5Zn-0.5Cu-0.1Sm alloy has the best protection capability based on its electrochemical capacity value with 2809.80
Ahr/kg and 98% current efficiency. Based on previous research, the addition of samarium to Al-5Zn-0.5Cu alloy results in SmCu₄Al₃ precipitates after the solidification process[3]. The presence of these precipitates results in a difference in potential values between the aluminum matrix and SmCu₄Al₃ precipitates, which increases galvanic corrosion occurrence in alloys.

The addition of samarium by 0.02 wt% in the sacrificial anode alloy results in a greater electrochemical capacity value with a value of 2604.01 Ah/kg compared to the sacrificial anode of aluminum alloy with the same amount of indium addition with a value of 2398.98 Ah/kg. The larger electrochemical capacity value indicates that the anode protection capability of the samarium alloy sacrifice is superior to the indium alloy. Based on the standards used, the minimum electrochemical capacity of the aluminum alloy sacrificial anode is 2500 Ah/kg[9]. After electrochemical test performed, only alloy with the addition of 0.02 wt% and 0.1 wt% samarium meets this prerequisite.

Table 2. Electrochemical performances of the alloys.

| Alloys | OCP (V vs SCE) | CCP (V vs SCE) at Different Current Densities (mA/cm²) | Capacity (Ahr/kg) | Efficiency (%) |
|--------|----------------|----------------------------------------------------|-------------------|----------------|
|        |                | 1.5  | 0.4  | 4    | 1.5 |                |                   |                  |
| A      | -0.913         | -0.735 | -0.715 | -1.033 | -1.047 | 1852.83 | 65.08 |
| B      | -0.911         | -0.890 | -0.599 | -0.649 | -0.610 | 2604.01 | 91.00 |
| C      | -0.884         | -0.834 | -0.755 | -0.897 | -0.914 | 2809.80 | 98.00 |
| D      | -0.942         | -0.779 | -0.748 | -0.681 | -0.553 | 2398.98 | 84.00 |

Anode potential measurement during efficiency test can be seen in Table 2. The open circuit potential (OCP) and the close circuit potential (CCP) of aluminum alloy with samarium addition showed more positive potential compared to the other alloys. However, the potential value obtained from the measurement shows decreasing and increasing at each measurement, this is due to the current from the external power source during the testing of the sacrificial anode efficiency which affects the work and potential value of the sacrificial anode. Wen et al. showed that lower fluctuation of CCP value implies the uniform corrosion, corresponding to the high anode efficiency[11]. According to Pautasso et al., low voltage aluminum sacrificial anode would have to supply a working potential around -0.8V vs SCE, because at this range of potentials the amount of hydrogen liberated is highly reduced and steel is still protected[2]. In this research, the most suitable candidate for low voltage aluminum anode is Alloy C with 0.1 wt% samarium addition, because it has OCP and CCP around -0.8V vs SCE. Furthermore, compared to aluminum anode with indium doping, alloy with samarium addition has better electrochemical performance for low voltage anode.

3.3 Macrostructure Analysis
The macro structure photographs in Figure 1 will present the physical differences produced by the sample of aluminum sacrificial anodes given the addition of samarium and indium alloys. The following are photos taken after weight loss testing and cleaned using a solution of 20 grams of CrO₃ and 30 ml of H₃PO₄ per liter of water for 10 minutes at 80°C. Based on four samples tested for efficiency, the most striking difference is that the macro structure changes to be rougher and more perforated. Samples with addition of samarium have a blackish appearance after testing, while samples with the addition of indium have silver appearance as tested. This is due to differences in the alloying elements used in casting the sacrificial anode. Based on the observations, the Al-5Zn-0.5Cu-0.1Sm alloy has a more even black color appearance compared to other samples with the addition of different samarium concentrations. This indicates that the Al-5Zn-0.5Cu-0.1Sm alloy has more uniform corrosion on its surface. On the other hand, three other samples are still visible in silver. This silver colored area shows no uniform corrosion throughout the surface of the sacrificial anode. The addition of samarium to the aluminum alloy anode sample causes the corrosion on the sacrificial anode to worsen up to the concentration of 0.1 wt% samarium. This occurs due to the segregation of samarium
at the grain boundary on the surface of the sacrificial anode which results in the surface concentration of Cl\(^-\) ions from seawater to rise on the oxide or passive layer of the sacrificial anode sample so that the passive layer becomes unstable and the surface of the sample becomes active[12].

![Figure 1. Macro Corrosion Photograph of the Alloys After Efficiency Test: (a) Al-5Zn-0.5Cu alloy; (b) Al-5Zn-0.5Cu-0.02Sm alloy; (c) Al-5Zn-0.5Cu-0.1Sm alloy; (d) Al-5Zn-0.02In alloy.](image)

On the other hand, the use of indium in the aluminum alloy sacrificial anode resulted in a uniform corrosion appearance on the sacrificial anode. Although the sacrificial anode macro structure is silver in color, the surface of this anode is corroded evenly. The form of corrosion that occurs on the surface of the sacrificial anode with the addition of indium is also different from the sacrificial anode with the addition of samarium. The sacrificial anode with indium has widely shaped corrosion throughout the surface, while with the addition of samarium, shaped as pitting corrosion.

4. Conclusions
Electrochemical behavior of Al-5Zn-0.5Cu alloy with varied samarium (Sm) addition of 0.02 wt% and 0.1 wt% compared to Al-5Zn-0.02In was investigated in this study. The highest value of electrochemical capacity and efficiency of sacrificial anode is found at Al-5Zn-0.5Cu-0.1Sm alloy with a value of 2809.80 Ah/kg with an efficiency of 98%. The use of samarium produces sacrificial anodes with better work efficiency compared to the addition of indium. Samarium increased the pitting resistance of aluminum, hence caused local corrosion. Al-5Zn-0.5Cu-0.1Sm alloy is the most potential alloy to be developed as a low potential sacrificial anode to replace commonly used aluminum sacrificial anode with indium addition.

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