Effect of samarium in Al-Zn-Cu as a micro-alloying element for low voltage sacrificial anode

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Abstract. Development of a low-voltage sacrificial anode for offshore structure has attracted increasing attention in recent years. The low-voltage operation can prevent the structure from overprotection and the resulting stress corrosion cracking. One of the efforts made to create this low-voltage sacrificial anode is by replacing indium as a conventional alloy with other elements such as copper, silicon, or gallium. Previous research showed that copper has the potential for low voltage properties, but the presence of interdendritic corrosion reduces the efficiency of the anode. The addition of samarium is aimed at a grain refinement that is expected to reduce the interdendritic phases’ size and disperses evenly. In this research, Al-Zn-Cu alloy with a variation of samarium composition by 0.1% Sm, 0.3% Sm, and 0.5% Sm was produced and it was followed by characterization which include metallographic test, differential scanning calorimetry, scanning electron microscopy, and energy dispersive spectroscopy. The results showed the dendrite size was reduced, in proportion with the addition of samarium, from 383 μm to 261 μm. Intermetallic Al-Cu-Sm phases were found in many interdendritic areas. Samarium also produced undercooling phenomena during the solidification process. Samarium contents below 0.3% acted as a grain refiner. Above that level, it will transform into a new phase. These findings indicate the Al-Zn-Cu-Sm alloy is a potential alloy to be developed into a low-voltage sacrificial anode.

1. Introduction

Presently, Indonesia is no longer a major oil exporting country. Decline in oil production from the proven reservoir is the main reason for this condition. It is more difficult to find the possibility of new resources, as the possible resources are located in deep sea regions. Most of the exploration resulted in the coastal and offshore area. Nevertheless, the marine environment is more corrosive than the onshore for the metallic structures of an oil platform. Therefore, it requires better protection to support the offshore infrastructure, one of which is a sacrificial anode.

From several types of available protection methods, the sacrificial anode is one of the corrosion protection mechanisms that can be used in a seawater environment. The sacrificial anode offers advantages because it is easier for installation and has a lower maintenance costs. Currently, the most widely used sacrificial anode is an aluminum-based anode of aluminum-zinc-indium alloy (Al-Zn-In). Al-Zn-In anodes produce excellent efficiency in its applications. Zinc addition is intended to make the
beta phase of aluminium (β aluminum) which makes the passive layer of alumina oxide easy to penetrate by the environment [1]. Meanwhile, the addition of indium will prevent the alumina's passive coating to readily re-form.

However, in some cases of applications of Al-Zn-In, failures as a result of stress corrosion cracking were found. This damage was due to a miscalculation of the sacrificial anode design that causes the steel structure, which should be protected, attacked by stress corrosion cracking. The addition of indium makes the potential of protected metals very low and reaches the evolution of hydrogen gas area in Pourbaix diagram. Several studies have examined if the replacement of indium with other elements could prevent the stress corrosion cracking. Other researchers has shown that gallium, silicon, and copper are the elements that made low-voltage aluminum sacrificial anode [2]. Aluminium-gallium (Al-Ga) operated within or near the desired potential range of -750 to -850 mV with anode efficiencies greater than 95%. Ga was found at elevated levels below the ground surface of uncorroded samples, with varying levels of Ga through the depth of corroded specimens [3].

A prior study by Ferdian et al. [4, 5] shows that copper is more efficient than silicon as an alloy for the low voltage sacrificial anode. The corrosion rate of this alloy increased with the addition of copper as its alloy. Furthermore, there is an inductance curve in the EIS test results indicating a decrease in oxide resistance of the aluminum. Copper makes the alloy potential more positive and makes the width of the loop even larger which indicates it takes longer time for re-passivation. Al-Zn-Cu alloy is chosen to be developed in this research due to the economical price and ease of obtaining it in the market. Based on literature review, several elements were already tried as an alloying element for the sacrificial anode. Gallium, silicon, and copper in aluminum anode showed increasing of steel potential protection and qualify the criteria to be a low voltage sacrificial anode as illustrated in Figure 1.

![Figure 1. Comparison of potential protection from various aluminum sacrificial anodes [3-5].](image)

Samarium is classified as a rare earth element and is known to have the ability as a grain refiner in aluminum alloys. According to Hu et al. [7], samarium can work as grain refinement by altering the morphology of the α-Al dendrite into a smaller grain. The changes also modified the morphology of eutectic silicon and iron-rich phase. Based on that finding, this research is expected to multiply the interdendritic area formed to make the intermetallic phase more evenly distributed in smaller sizes than without the addition of samarium. Another work by Hongxu et al. [8], shows that the addition of Sm elements could affect the morphology of eutectic silicon. The addition of 0.3% samarium in the alloy made the eutectic smoother than without samarium and made the phase more rounded. The effect of samarium in silicon eutectic modification is optimum until the addition of 0.6% Sm. A higher percentage of samarium addition can make eutectic silicon the original shape.

2. Methodology
The sample for sacrificial anode was made by a casting process. A resistant furnace was used with graphite crucible which heated at a temperature of 750 °C for 90 minutes. The stirring process of the aluminum was carried out using graphite bar, and the remnant of slag and impurities on the surface of molten metal was removed before pouring process. In order to achieve the target alloying composition, binary Al-10Sm was made as a master alloy and melted in a graphite crucible and then mixed with Al-5Zn-0.5%Cu. The alloying element is weighed to achieve the target for a quaternary alloy of Al-5Zn-0.5Cu-xSm. The casting product was characterized by several tests such as metallographic, Energy Dispersive Spectroscopy, and Differential Scanning Calorimetry.

3. Result

3.1 Differential scanning calorimetry
DSC experiments were carried out under a low nitrogen flow and cooling rate of 10 °C min⁻¹. They consisted of heating the sample up to 700 °C, holding it at that temperature for 10 min for homogenization, and finally cooling it down to room temperature. Figure 2 shows the DTA thermogram upon cooling for different samarium addition. Two solidification reactions occur successively at decreasing temperature. The nucleation of (α-Al) dendrites (refer to the first peak in Figure 2) and followed by the formation of rich samarium intermetallic phase as the second peak. The peak becomes distinctively clearer as the samarium level increases, as seen in thermogram for Al-5Zn-0.5Cu-0.5Sm. The addition of samarium also slightly shifted the precipitation temperature of α-Al solidification into the lower temperature.

Based on thermogram, two-phase transformation occur at a temperature of approximately 620 °C for α-Al solidification and 580 °C for samarium rich intermetallic phase. Analysis of the ternary phase diagram of Al-Zn-Sm showed no indication of high-temperature intermetallic phase precipitation, while analysis with ternary Al-Cu-Sm, the second peak could be associated with SmCu₄Al₁₁ phase. This temperature is near with the isothermal temperature of Al-Cu-Sm as shown in Figure 3 and conforms with SmCu₄Al₁₁ formation.

![Figure 2. DSC result from Al-Zn-Cu and Al-Zn-Cu-Sm.](image)

3.2 Microstructure

3.2.1 Metallography. The microstructural observation was conducted using a metallographic method using optical emission spectroscopy and scanning electron microscope (SEM). Microstructural observations were performed using optical microscopy (OM) for as cast and controlled cooling rate (DSC). All of the metallographic examinations is taken by the non-etchant process. It can be seen clearly, grain boundaries revealed with brighter colors. The intermetallics appear on grain boundaries
signed by white color. The intermetallic is formed at the grain boundary because the grain boundary is the last area that solidified during the dendrite formation as seen in Figure 4.

![Figure 3. Isothermal section at 500 °C of ternary Al-Cu-Sm phase diagram [10].](image)

![Figure 4. Effect of samarium in microstructure of Al-Zn-Cu with addition (a) 0% Sm, (b) 0.1% Sm, (c) 0.3% Sm and (d) 0.5% Sm.](image)

The alloy that contain 0.5 wt% samarium has many intermetallics in the grain boundary compared with 0.1 wt% and 0.3 wt% Al-Zn-Cu-Sm alloy. This indicates more samarium addition made a new intermetallic phase in the grain boundary with the other element. Zhi Hu et al. also found the similar result after 1% addition of Sm in AlSiCu alloy. They found two type of precipitate at 1% Sm addition. It indicated most of the samarium will bound with the other element rather than dissolved in the matrix [7].

Metallographic observations also show a decrease in the length of secondary dendrite arm spacing (SDAS). The average length of grain size that was formed before the addition of samarium was 383 μm.
while the observation after the addition of 0.5% wt samarium became 245 μm. Based on Figure 5, the most optimal addition is 0.3% samarium to produce finer SDAS. Above these concentration, DSC and metallography analysis showed that Sm started to form a new intermetallic phase. The same phenomenon was also found in Al-Si-Mg alloy which showed a silicon phase modification at 0.6% Sm [11]. This result indicated the potential for better intermetallic dispersion from the as-cast product.

Figure 5. Effect of samarium addition in Al-Zn-Cu-xSm to SDAS.

Figure 6. Elemental mapping of Al (red), Zinc (blue), Yellow (copper) and Samarium (purple).

3.2.2 Energy dispersive spectroscopy: element mapping. Energy dispersive spectroscopy test performed to the sample with the highest samarium content (0.5% Sm). All items of the alloy are spread evenly on the microstructure as seen in the elemental mapping results in Figure 6. Several areas in Al element mapping result showed less aluminum content in the interdendritic region. On the contrary, these area has a more abundant Sm and Cu than aluminum. Zinc is spread evenly in an aluminum matrix. This
condition is caused by the high solubility level of zinc in aluminum. Copper still gathered around, and bound with, the samarium in the interdendritic area form an intermetallic. It proved the possibility of SmCu₄Al₁₁ in this alloy as predicted by DSC result.

4. Conclusion
Samarium acted as grain refiner in Al-5Zn-0.5Cu-xSm alloy. Differential scanning calorimetry showed an intermetallic SmCu₄Al₁₁ formed at temperature 580 °C and the α-Al solidification formation shifted to the lower temperature after an addition of 0.1% Sm in the alloy. The most efficient of samarium addition for grain refinement is 0.3% Sm. It could reduce the secondary arm spacing size by approximately 25%. Secondary arm spacing reduced from 383 μm to 261 μm after addition of 0.3% Sm. A higher samarium content increases the intermetallic formation in the grain boundary of Al-Zn-Cu-Sm alloy.

References
[1] Muazu A and Yaro S 2011 J. Miner. Mater. Charact. Eng. 10(2) 185–98
[2] Monzel M William J Druschitz Alan P 2014 Maxfield Corrosion 4284
[3] Baker D S 2015 Virginia Polytechnic Institute and State University
[4] Ferdian D Pratesa Y Togina I and Adelia I 2017 Proc. Eng. 184 418–22
[5] Ferdian D Pratesa Y Togina I 2017 IOP Conf. Ser. Mater. Sci. Eng. 12026
[6] Ma-Li H B Weili L I Hongjie Z Yonggui Y 2010 J. Chinese Soc. Corros. Prot. 4 2–5
[7] Hu Z Yan H and Rao Y S 2013 Trans. Nonferrous Met. Soc. China Eng. 23(11) 3228–34
[8] Qiu H Yan H and Hu Z 2013 J. Alloys Compd. 567 77–81
[9] Liang S M and Schmid-Fetzer R 2016 Calphad Comput. Coupling Phase Diagrams
Thermochim. 52 21–37
[10] Riani P Arrighi L Marazza R Mazzone D Zanicchi G and Ferro R 2004 J. Phase Equilibria
Diffus. 25(1) 22–52
[11] Qiu H Yan H Hu Z 2013 J. of Alloys and Compd. 567 77-81