The Effect of Neodymium on the Solidification Process of Al-5Zn-0.5Cu Alloy Sacrificial Anode

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Abstract. The effect of the addition of neodymium rare earth on Al-5Zn-0.5Cu alloy was investigated with Optical Microscope (OM), Differential Scanning Calorimetry (DSC), and Cyclic Polarization. The content variable of neodymium tested was 0.1wt%, 0.3wt%, dan 0.5wt%. Observation with OM was conducted to see the changes of the SDAS and the precipitate formation. DSC was used to identify the phase transformation and solidification process of the intermetallic phase. Cyclic Polarization was used to know the corrosion characteristics of Al-5Zn-0.5Cu-xNd. The presence of neodymium formed precipitates on the grain boundary which made shorter SDAS. Addition of neodymium as an alloying element of Al-5Zn-0.5Cu sacrificial anode may decrease pitting corrosion resistance and reduce the size of the loop. This behavior will be more preferable for Al Anode because the indication of more uniform attack.

Keywords: Solidification, Rare Earth, Neodymium, Sacrificial Anode, Aluminium Alloy

1. Introduction
Pautasso et al. (1998) explain the tendency for hydrogen embrittlement (HE) and stress corrosion cracking (SCC) on HSS steel structures as a result of overprotection [1]. Overprotection occurs because the potential value of Al-Zn-In reaches -1.15 V vs. SSC [2]. The properties of aluminum sacrificial anodes include high current efficiency, low density, and long life usage [3]. Pure aluminum sacrificial anodes cannot be used because the sacrificial anode will immediately form a passive γ-Al₂O₃ layer on its surface [4]. Sacrificial anodes that form a passive layer will make the corrosion attack which should attack the sacrificial anode to attack the supposedly protected structure. This indicates that the formation of a passive layer on the sacrificial anode will make the sacrificial anode not work properly. It is also known that the addition of Zn will damage the stability of Al₂O₃ layer forming which will facilitate the process of corrosion [5]. The addition of the Zn element will destroy the passive layer on the anode surface with its second phase particles. These second phase particles have a certain volume fraction known as β-phase [6]. Studies show that rare earth metals as micro-alloying exhibit a beneficial impact on the mechanical properties of aluminum alloys. Studies are showing that Nd is primarily distributed in the form of intermediate compound AlCuNd which gives a resistive force on grain boundaries and increased the performance of Al 2A70 alloys at high temperatures [7]. The α-Al phases tend to corrode without the protection of the Al₂O₃ layer. The corrosion product layer grows with the dissolution of the η-Zn and α-Al phases. The corrosion resistance decreases as the immersion
time increases due to the destruction of the Al2O3 protective layer, selective corrosion of alloys, and the formation of defects in the corrosion product layer [8]. According to Minliang Su et al., the as-cast HPDC AlNd44 alloys exhibit relatively good corrosion resistance strength, which is due to the presence of Al-Nd intermetallic phases that converge at the grain / dendritic boundary and act as a corrosion barrier. After annealing at temperatures above 573K, the corrosion rate increases with changes in the microstructure, i.e., the disintegration of reticular structures near the grain / dendritic boundaries [9].

2. Experimental method

2.1 Sample Preparation
The raw materials for this test were high purity of Al, Zn, Cu, and Nd. Each of element was melted with Resistance Furnace at temperature 750°C for 30 minutes after preheated at 400°C to make Al-Zn-Cu alloy. The melting of metals is aided by a graphite stirrer to allow the melt to homogenize appropriately. When the molten aluminum is completely dissolved, the dross was cleaned, and the metals were cast into the graphite mold. Neodymium was inserted by using Al-10 Nd master alloy. This master alloy was made at temperature 800°C for 30 minutes. a The process of adding Nd to the melt must be done very quickly due to the high reactivity of neodymium with oxygen. Casting process of Al-5Zn-0.5Cu-xNd starts with melting the Al-5Zn-0.5Cu alloy at 720°C and held for 10 minutes. Afterward, Al-10Nd is added to the melt at 730°C. The melting metals is homogenized for 5 minutes and held for 10 minutes. Then the Al-5Zn-0.5Cu-xNd alloy is poured into the mold.

2.2 Characterization of Al-5Zn-0.5Cu-xNd Samples.
In this stage, each sample is characterized using Optical Microscope (OM), Differential Scanning Calorimetry (DSC) and Cyclic Polarization with metroohm potentiostate (CP). OM is used to see the grain boundary shape, the precipitate formed, and the length of the SDAS. DSC is used to see the phase transformations that have formed during the solidification process. This DSC experiment was measured with 10°C/minutes scanning rate. Polarization test is used to determine the corrosion properties of alloys. Cyclic polarization was conducted in 3.5% Sodium Chloride solution at ambient temperature. A standard three-electrode system was used for the potentiodynamic test. Graphite as a counter electrode and Ag/AgCl electrode as a reference. The OCP procedure was done for 15 minutes before starting the experiment.

3. Results and discussion

3.1 Differential Scanning Calorimetry (DSC).
DSC test result for Al-5Zn-0.5Cu-0.5Nd showed in Figure 1. The result showed the cooling process from temperature 670°C to 450°C. The cooling speed of this solidification process is 10°C / min. Fig 1 showed the starting point of the formation of the α-Al phase at 622°C. Then, a great release of energy happened until temperature 620°C (2), so the formation of the α-Al phase occurs in this temperature. If we compare with the Al 5Zn 0.5Cu result, the α-Al phase solidification is slightly shifting from 625 to 622 °C.

3.2 Optical Microscope
Microstructural observations were performed using Zeiss Primotech optical microscope on Al-5Zn-0.5Cu material with variations of 0.1 Nd, 0.3 Nd, and 0.5 Nd addition. The sample is an as-cast sample. Microstructures of Al-5Zn-0.5Cu alloys, Al-5Zn-0.5Cu-0.1Nd, Al-5Zn-0.5Cu-0.3Nd, and Al-5Zn-0.5Cu-0.5Nd is shown in Figures 2. Based on the microstructural observations in Figure 2, clear grain boundaries with lighter colors than their matrices can be observed. The precipitate may also be visible in white on the grain boundary. 0.5 w.t% Nd addition had more precipitates at grain boundaries than neodymium addition of 0.1 and 0.3 w.t%. This phenomena suggests that the formation of precipitates
Figure 1. A slightly shifting of $\alpha$-Al phase peak.

Figure 2. As-cast microstructure of a) Al-5Zn-0,5Cu, b) Al-5Zn-0,5Cu-0,1Nd, c) Al-5Zn-0,5Cu-0,3Nd, and d) Al-5Zn-0,5Cu-0,5Nd (Magnification 50x).
at the grain boundary is directly proportional to the number of neodymium additions, as more neodymium is added to the alloy, the more precipitates are formed at the grain boundaries. The size of Secondary Dendrite Arm Spacing (SDAS) area is also smaller 0.5 wt% of Nd. It is an indication that the Nd acted as the grain refinement. The 0% Nd SDAS is around 200 µm, then it was decline to around 65µm after addition of 0.5% Nd.

3.3 Cyclic Polarization
Figure 3 showed the Al-5Zn-0,5Cu alloy passivation region will be shorter with the increase of neodymium element alloying. A study by Junguan He et al. [10] showed that the elongated form of precipitate would tend to undergo pitting corrosion, whereas the round precipitates are more likely to undergo uniform corrosion. In Figure 3, it is clearly seen the passive region is smaller after Neodinium addition. It is indication that the pit is more shallow than Al Zn Cu alloy. It is also an indication Nd make the corrosion is more uniform.

![Figure 3. Cyclic polarization showed narrowing of loop with Nd addition.](image)

4. Conclusion
The formation of precipitates at the grain boundaries is directly proportional to the number of neodymium additions, the more neodymium added to the alloy, the more precipitates formed at the grain boundaries. The function of adding neodymium elements is as a grain refiner. The effect of the addition of neodymium elements as much as 0.1%, 0.3%, and 0.5% decreases the length of SDAS. The addition of neodymium decreased pitting corrosion resistance and make the loop smaller. It is a good indication for the shallower pit which is more beneficial for sacrificial anode.

Acknowledgment
We would like to give our thanks and appreciation to Hibah PITTA 2018 Nomor: 2413/UN2.R3.1/HKP.05.00/2018 for supporting the funding in this research.

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