

Microscopic Observation of Pattern Attack for Different Chemical Composition of Aluminium Alloy Sacrificial Anode by Aggressive Ions on Finished Surface

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Abstract: This paper presents the results of a microscopic observation on submerged finished surface for different alloy composition of aluminium alloy sacrificial anode. There are 3 samples of aluminium alloy with different condition, that surface of sacrificial anode were attack by an aggressive ion such as chloride along grain boundaries. In addition, results of microanalysis showed that the elements chemical composition has been tested in this study. Experimental tests were carried out on polished surface aluminium anode exposed to seawater containing aggressive ions in order to observe of pattern corrosion attack on corroding surface of anode. Results have shown, at least under the present testing of aluminium (Al), zinc (Zn), magnesium (Mg) and stanum (Sn) still present on surface after 35 days immersed in stagnant seawater and it was believed that the surface of the aluminium alloy remained in active conditions. Because alloying element such as Sn is cathodic to aluminium, its cation will plate out on the aluminium surface, according to an electrochemical exchange reaction with aluminium. Therefore this exchange reaction locally separates the oxide film on the surface of aluminium.

Keywords: Corrosion, Aggressive Ions, Sacrificial Anode, Aluminium

I. INTRODUCTION

Offshore steel structures in seawater are now routinely cathodically protected. This protection consists of an impressed direct current between the structure and the anodes. The current polarizes the structure, shifting its potential. The process leads to impress electrons on the cathode, say steel surface, suppressing oxidation of ion, i.e the corrosion process [1]. Recently, the most commonly studied metals for cathodic protection systems have been alloys of magnesium, zinc and aluminium [2].

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Aluminium alloy are preferentially selected for cathodic protection of steel object due to high current efficiency, low specific weight low cost of alloy. However pure aluminium will easily form a passive oxide film on its surface when it is exposed aqueous environment, so the element such as stanum, magnesium and zinc should be added as alloying elements for the purpose to activate the passive film on the aluminium surface.

When the surface of aluminium alloy exposed to the dry air, the passive film on its surface will be form to avoid the oxidation process on the surface. The thickness of the film will be increase when exposed to the high dry air temperature [3]. When exposed in the water, the thickness of the film was highly increased and changes depend on the temperature [3]. The growth rate of the film follow the logarithm on time depends on the temperature, oxygen content and ion presence in the solution.

This paper presents a thorough study of the effect of chemical composition on the microscopic observation of pattern attack by aggressive ions. Chloride ions present in seawater will be attacked the aluminium surface by electrochemical exchange reaction with aluminium. The discontinuity of grain structure of the aluminium alloy will be enhanced the corrosion mechanism through electrochemical exchange with respect to the bulk grain [4].

II. EXPERIMENTAL

A. Material Preparation

The principal aim of this present study is to investigate the pattern attack of aggressive ion on finished surface for different chemical composition of aluminium alloy submerged in stagnant seawater at ambient temperature. Raw materials were used in this study are commercial pure Aluminium (99.8%), Zinc (99.8%), Magnesium (99.9%) and Stanum (99.9%). Raw materials in the ingot forms were cut into the small pieces and washed prior to melt using a tilting furnace at 850°C. The molten alloy was poured in a preheated split cast iron mold (figure 1a) and slowly cooled at atmospheric environment. A casting product is as shown in figure 1b. Table 1 shows the result of chemical compositions of the alloy after analyzed using spark emission spectroscopy.

TABLE I
THE CHEMICAL COMPOSITION OF THE ALLOY (Wt %)

Sample	Analyzed chemical Composition wt (%)			
	Al	Zn	Mg	Sn
A	Balance	4.315	-	0.029
B	Balance	4.670	-	1.312
C	Balance	4.662	2.080	1.408

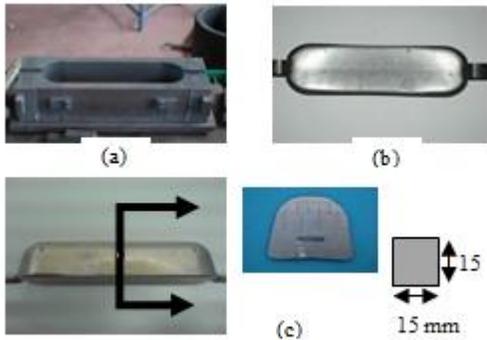


Figure 1: (a) Cast iron mold (b) Aluminium casting product (c) Cutting part

The samples were cut into the square form with dimension of 15mm x 15mm from a cast product as shown in Figure 1c. There are 3 different chemical composition of aluminium alloy samples of aluminium alloy were used in this study. The samples were mounting prior to testing. Careful and meticulous surface preparations are necessary to reveal the important details of the microstructure. The samples surface must first be ground up to grit 4000 silicon carbide paper and then polished with 4µm and 1µm diamond pastes to a smooth and mirrorlike finish. The microstructures were revealed by a surface of treatment using Keller's etchant, and then the microstructure is observed using image analyzer.

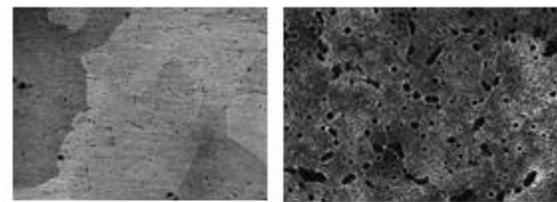
B. Immersion Test

Three different samples were immersed separately in the sea water for the period of 35 days exposure time. At the end of the experiment, the anode samples were cleaned by tooth brush and wetted cotton with 5% H₂NO₃, rinsed with water and dried. The pattern attack of the surface samples were observed using image analyzer and FEI S600 Scanning Electron Microscope (SEM).

III. RESULT AND DISCUSSION

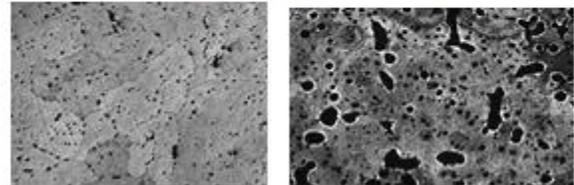
A. Surface Morphology

The present results of this study give an insight to the relationship between aluminium containing alloying elements and microstructural examination. It was observed that the aluminium alloys were subjected to general and localized attack of different degree. The localized attacks were crevice and pitting corrosions; but of this, pitting corrosion was prevalent. It was noted that the severity of the attack is irrespective of the tin concentration and also the present of magnesium. It was observed that the sample with 0.029% tin showed the least susceptibility to the corrosion attack (Figure 2). The anode sample with 1.312% tin was found to be most susceptible to attack (Figure 3) and it was followed severe attack by sample containing magnesium and tin (Figure 4).



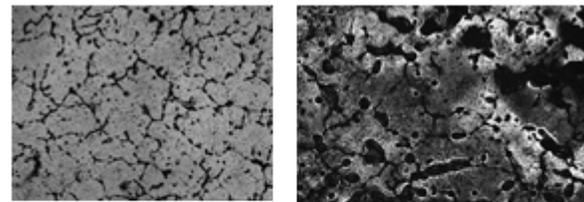
(a) Before exposure (b) After exposure

Figure 2: Micrograph of Al-Zn with 0.029% Sn prior and after exposure, 50X



(a) Before exposure (b) After exposure

Figure 3: Micrograph of Al-Zn with 1.312% Sn prior and after exposure, 50X



(a) Before exposure (b) After exposure

Figure 4: Micrograph of Al-Zn with 2.080 Mg and 1.408% Sn prior and after exposure, 50X

The distribution of the zinc and magnesium in the aluminum matrix must have been heterogeneous. This situation could have set up galvanic cells in some portions of the aluminum resulting in the pockets of localized attacks characteristic of pitting or crevice corrosion. From physical metallurgy and phase diagrams of aluminum alloys, it is clear that tin is negligibly soluble in aluminum. Tin has been observed to have a solubility of less than 0.01 wt% in the aluminum matrix at the melting point of approximately 231.2°C. It is suspected that galvanic cells set up between the tin and the aluminum matrix results in dissolution of aluminum or zinc and magnesium in the vicinity of the tin when they are soaked in seawater. The consequence of this phenomenon is that the networks of the passive oxides of the aluminum alloy are broken down thus increasing the corrosion attack.

EDAX Analysis of the alloy surface

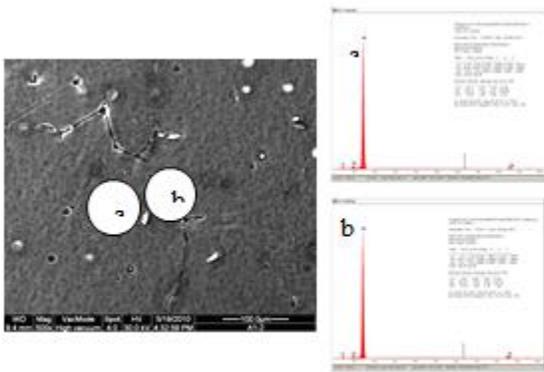


Figure 5: SEM photograph and EDAX analysis of alloy sample A

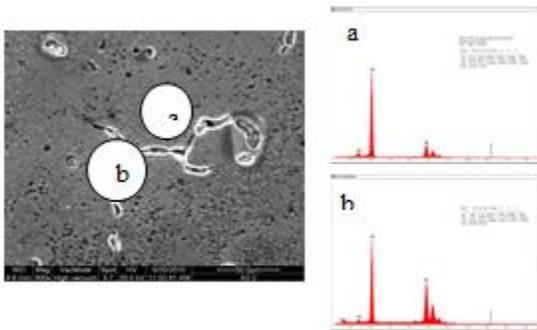


Figure 6: SEM photograph and EDAX analysis of alloy sample B

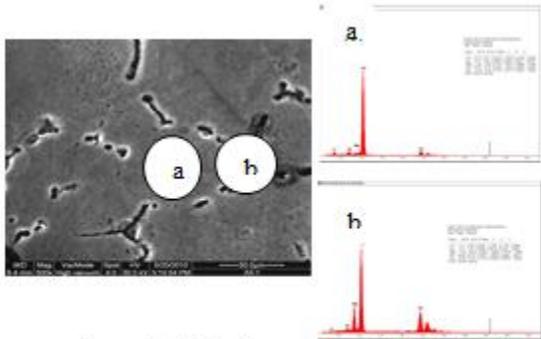


Figure 7: SEM photograph and EDAX analysis of alloy sample C

Figure 5 shows a semiquantitative EDAX analysis on the sample with 0.029% tin after immersed in the sea water. The EDAX result showed that the Al, Zn and Oxygen present at both location denoted “a” and “b”. It was suspected that the thinning oxide film formed the surface. The content of Zn and oxide are slightly same for surface and grain boundary area. Zinc is a more active metal than α -Al. So Zn precipitates can be acted as corrosion center and cause the initiation and propagation of pitting corrosion.

Figure 6 shows an EDAX analysis on the corroded surface of the aluminium alloy with 1.312%Sn. The EDAX result indicates that the surface at position a and grain boundary at position “b” all contain Al, Zn and Sn element but the content of Sn in the grain boundary is the highest than of the surface. The Sn element of the alloy may involve the dissolution-precipitation process and the precipitation of Sn should reach

a critical value that lead to the corrosion with the grain boundary. The grain boundary of the alloy can be possible explained by considering passivation in the alloy as a dynamic process. The oxide film is expected to dissolve and a fresh film is expected to appear, through at a much slower rate. This is depending on the dissolved cations which might redeposit on the surface as hydroxides (5). During the dissolution-precipitation process, the Sn ions are incorporated in the oxide film. Yet a further mechanism of incorporation is at flaws themselves, stannum and zinc being noble may become deposited on these sites

Figure 7 shows the EDAX analysis on the corroded surface of the aluminium alloy with 2.08%Mg and 1.408%Sn. The EDAX results indicate that the surface at point a and grain boundary at position b all contain Al, Zn, Mg and Sn element but the content of Mg and Sn in the grain boundary is the highest than the surface. It has been documented that the main precipitates phase is $MgZn_2$ particles in aluminium alloy containing both Zn and Mg, and the corrosion potential of the bulk $MgZn_2$ is more negative than that of α -Al (6). So $MgZn_2$ precipitates can be acted as corrosion center and cause the initiation and propagation of pitting corrosion along grain boundary. The presence of higher Sn at grain boundary causes the dissolution- precipitation process and the precipitation of Sn should reach a critical value that lead to the corrosion with the grain boundary. It means that the high presence of Mg and Sn in the grain boundary cause the high of pitting point that accelerate the corrosion behavior.

IV. CONCLUSION

The microscopic observation of aluminium alloy with different chemical composition immersion in sea water at 36 days were developed using optical microscope, SEM and EDAX. Most of the pitting point was present along the grain boundary. The presence of Zn, Mg and Sn cause the acceleration of corrosion process. The pitting predominates the mainly corrosion process controlled by the activation of the precipitates particles in the alloy at the initial stage of corrosion.

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