Microscopic Observation of Pattern Attack by Aggressive ions on Finished Surface of Aluminium Alloy Sacrificial Anode

Zaifol Samsu, Muhammad Daud, Siti Radiah Mohd Kamarudin, Nur Ubaidah Saidin, Azali Muhammad, Mohd Shaari Ripin, Rusni Rejab, Mohd Shariff Sattar

Material Technology Group, Industrial Technology Division, Malaysian Nuclear Agency



Abstract

This paper presents the results of a microscopic observation on submerged finished surface of aluminium alloy sacrificial anode. 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 condition, that surface of aluminium alloys were attack by an aggressive ion such as chloride present in seawater along grain boundaries. In addition, results of microanalysis showed that the corrosion products on surface of aluminium alloy have Al, Zn, Mg and O element for the whole surface of sample meanwhile within the pit was consists of Al, Mg, Zn, O and S element.

Keywords: Aggressive ion, Sacrificial Anode, Pit

Abstak

Penulisan ini membentangkan hasil pemerhatian mikroskopik terhadap permukaan akhiran terendam gabungan aluminium anoda korbanan. Ujian makmal telah dilakukan terhadap permukaan aluminium anod yang dilicinkan yang telah dimasukkan ke dalam air laut yang mengandungi ion agresif untuk mengamati pola serangan kakisan pada permukaan anoda yang terkakis. Keputusan kajian menunjukkan, sekurang-kurangnya di bawah keadaan ujian ini, permukaan anoda korbanan telah mengalami serangan ion yang agresif seperti klorida di sepanjang batas butir. Selain itu, keputusan mikro menunjukkan bahawa produk kakisan pada permukaan aluminium gabungan mempunyai Al, Zn,Mg dan unsur O untuk sampel itu dan dalam lubang itu terdiri dari Al, Zn, O dan unsur S.

Katakunci: Ion agresif, Anod Korbanan, Lubang

INTRODUCTION

Sacrificial anodes are the galvanic anodes that prevent corrosion of steel when coupled with the steel. During cathodic protection, the sacrificial anode, say aluminium is ejected into the environment as its ion. 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). 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 form a passive oxide film on its surface when it is exposed aqueous environment, so the element such as stanum and zinc should be added for activation the passive film. Numerous studies have been carried out to study the corrosion behavior about this alloy.

This study was focus on the microstructure analysis of the aluminium alloy immersed in sea water. The characteristic of the before and after immersed sample have been compared by each other. Ever since, a great amount of studies have been carried out due to its excellent mechanical properties reached after age hardening (3) and (4) and for the combination of low density and high strength, which have made of the Al-alloys the primary material, to be used in the aircraft and automotive industries.

For Al-Zn-Mg-Sn sacrificial anode, the corrosion behavior is expected to be related to the multielement and the distribution in the microalloy. Pitting corrosion was occurring at local site of passive film breakdown. Pitting occurs when one area of metal becomes anodic with respect to the rest of the surface. Pitting is one of the most insidious forms of corrosion. Pits are generally small and often remain undetected by simple visual examination (5)

PROCEDURE

Material Preparation

The principal aim of this present study is to investigate the pattern attack of aggressive ion on finished surface of Aluminium alloy submerged in stagnant seawater. The analyzed chemical compositions of alloy in this study were done using spark emission spectroscopy and the result is shown in the table 1. 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 according to weight required and washed prior to do the melting process by put in them in a crucible furnace in tilting furnace at 850°C. The molten alloy was poured in a preheated cast iron mold (figure 1a) and slowly cooled at room temperature. A casting product is as shown in figure 1b

| Sample | Analyzed chemical Composition wt (%) | | | |
|--------|--------------------------------------|-------|------|-------|
| | Al | Zn | Mg | Sn |
| A | Balance | 4.662 | 2.08 | 1.048 |

Table 1: The chemical composition of the alloy (wt %)

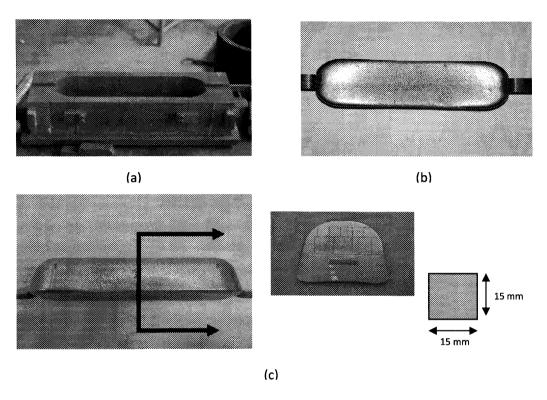


Figure 1: (a) Cast iron mold

(b) Aluminium casting product

(c) Cutting part

The samples were cut 15 mm square from a certain part of casting product as shown in Figure 1c. 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 $4\mu m$ and $1\mu m$ 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.

Immersed test

The samples were immersed in the sea water contained in the beaker at the time of 35 days. The corrosion products of the samples were clean out by tooth brush and wetted cotton with 5% H_2NO_3 , then rinsed by ethanol. The microstructure of the corroded surface samples were observed using image analyzer and examined using FEI S600 Scanning Electron Microscope (SEM).

RESULT AND DISCUSSION

Surface Morphology

The microstructure of the alloy is shown in Figure 2(A). The alloy is mainly consisted of α-Al matrix with precipitates on continuous or semi continuous network of grain boundaries. The microstructure of an alloy can contain multiple phases, and the distribution and amount of the second phase are controlled to develop desired properties, for example, increased strength or toughness (3). The segregation along grain boundary appears as Sn composition and was found the formation of globules (black dots) in the aluminum matrix. There are no quaternary phase diagrams for Al-Zn-Mg-Sn is available in the literature. However phase diagrams for Al-Sn, Al-Mg and Al-Zn existed and have been reported. Also the ternary phase diagrams for Al-Zn -Mg are available and have been reported; these diagrams give some clues to the possible structure of the Al-Zn-Mg phase diagram. The Al-Zn and Al-Mg phase diagrams show that Zn and Mg are both soluble at high temperature and still very soluble (about 5% for Zn and 2% for Mg) at room temperature. This is probably why its globules were found (black dots) in the aluminum matrix.

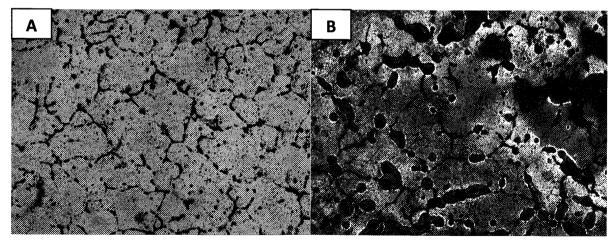


Figure 2: The optical imagine of the sample before (A) and after (B) immersed in sea water

Figure 2 (B) show the representative corroded surface of the alloy after immersed in sea water for 35 days. Pit was appeared at point along the grain boundaries (Figure 3). Corrosion was happen in homogenous pattern without a strong passive film on the alloy surface. The electrochemical reaction mechanism of the aluminum alloy in sea water is:

```
Anode dissolution process

Al \rightarrow Al^{3+} + 3e-
Cathode reduction process

O_2 + 2H_2O + 4e^- \rightarrow 4OH^-

Overall reaction:

Al + 2H_2O + Cl^- \rightarrow Al(OH)2Cl + 2H^+ + 3e-
```

Actually sodium chloride (NaCl) present in seawater was ionized into cation of sodium (Na+) and anion of chloride (Cl-). An ion chloride (Cl-) was act as an aggressive ion and favor attack on matrix and grain boundary of the alloy. Aluminium ion was act with hydroxide ion to produce the aluminium oxide that was appeared as corrosion product on the alloy surface. Gas hydrogen was release as a bubble during the reduction process.

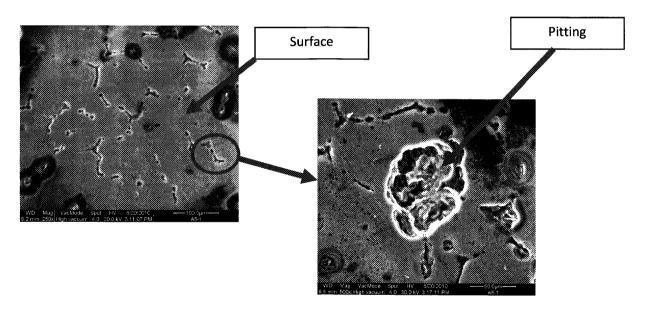


Figure 3: Location of surface and pitting point

CONCLUSION

Overall observation through optical and SEM shows that the pattern of corrosion attack was initiated along grain boundaries and some pits also present on the surface due to electrochemical reaction mechanism between alloy surface and aggressive ion environment.

ACKNOWLEDGEMENT

I would like to thanks to Dr Azali Muhammad, Head of Material Technology Group, Dr Abd Nassir Ibrahim, Director of Industrial Technology Division and also to all MTEG staff who are directly and indirectly involved of this project

REFERENCES

- 1. S.M.A. Shibli, V.S., Gireesh, S. George, Surface catalysis based on ruthenium dioxide for effective activation of aluminium sacrificial anode, Corrosion Science 46 (2004) 819-830
- 2. W.R. Osorio, C. Marina and A. Garcia, *J. Alloys Compd.* 397 (2005), pp. 179–191. View Record in Scopus | Cited By in Scopus (32)
- 3. J. Lendvai, *Mat. Sci. Forum* 217–222 (1996), pp. 43–56. Full Text via CrossRef | View Record in Scopus | Cited By in Scopus (52)
- 4. X.J. Jiang, B. Noble, B. Holme, G. Waterloo and J. Tafto, *Metall. Mater. Trans.* A31 (2000), pp. 339–348. View Record in Scopus | Cited By in Scopus (24)
- 5. J.R. Davis Davis & Associates, Corrosion Understanding and basics, page 32