CORROSION BEHAVIOUR OF ALUMINUM ALLOY IN SEAWATER

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ABSTRACT

Many different types of destructive attack can occur to marine structures, ships and other equipments used in sea water service. Year upon year the cost of marine corrosion has increased until it is estimated today at 4 % of the Gross National Product. Aluminium alloys are important materials and commonly used in marine applications. In the current research we are simulating a ship cargo container, which carries corrosive aqueous material. In this study different types of aluminum were subjected to aqueous corrosion in salt spray chamber and normal seawater container. Natural products (such as starch) were used as corrosion inhibitors for various metals and alloys in aggressive marine environment. In order to study the corrosion behavior of aluminum alloy AA6063 in seawater, the electrochemical behavior of aluminum alloys was investigated with different inhibitor concentrations, using electrochemical potentiodynamic reactivation (EPR), potentiodynamic polarization and electrochemical spectroscopy (EIS). The morphology study was carried out to observe the development of thin film on the specimen and this study was performed using Scanning Electron Microscopy (SEM). The values of activation energy confirm this result. EIS data showed that the mechanism of corrosion depends on inhibitor concentration.

Keywords: Corrosion, Marine Environment, Aluminum alloy.

1. INTRODUCTION

Many ship superstructures and liquid cargo containers are made of aluminum due to its low weight and acceptable strength. The most popular aluminium alloys for use in corrosive environments such as seawater are the 5xxx and 6xxx series alloys, which demonstrate adequate strength and excellent corrosion resistance. These series are highly suitable in various marine structures, machinery and port buildings. Alloy 6063 is a heat treatable aluminium-magnesium-silicon alloy. It provides good combination of extrudability and mechanical properties. It also responds well to polishing chemical brightening, anodizing and dyeing.

Ship cargo containers are exposed to sea environment. Not only the outside of the cargo containers are exposed to corrosive environment, the internal compartments are also exposed to corrosive aqueous media.

Marine corrosion is a perennial problem not only to moving vessel but also ports and anything kept in the sea or exposed to sea environment for a period of time. Corrosion is fundamental process which plays an important role in economics and safety. Apparently, corrosion cannot be avoided, but its severity can be reduced to a lower magnitude.

The term 'aqueous corrosion' describes the majority of the most troublesome problems encountered when metal material is in contact with sea water. Various methods have been employed to reduce corrosion. Several techniques and methods have been developed to combat corrosion efficiency are continually being sought after, as a result of exorbitant amount spent on corrosion annually (Abd El Rahim et al. [1], Bethencourt et al. [5]). The use of inhibitor for the control of corrosion of shore and offshore metal and alloys which are in contact with aggressive marine environment is an accepted practice.

Benzoate compounds offer interesting possibilities for corrosion inhibition and are of particular interest because of their safe use and high solubility in water (Rosliza and Wan Nik [10]).

Corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared to other preventive methods. Normally inhibitors are chemicals that interact with a metallic surface, or the environment this surface is exposed, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface by forming a film and reducing corrosion.

1.1 Corrosion Inhibitors

Inhibitors have always been considered to be the first line of defense against corrosion. Several corrosion inhibitors are available today. The objective of this study was to evaluate the effectiveness of sodium benzoate as an inhibitor to slow down or prevent corrosion. This project involves the use of gravimetric measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) to evaluate inhibitive action of sodium benzoate on corrosion behavior of AA6063 aluminium alloy in seawater. The electrochemical measurements showed that the presence of sodium benzoate as an inhibitor significantly decrease the weight loss, corrosion current densities (i_{corr}), corrosion rates and double layer capacitance (C_{dl}), whilst increasing the polarization resistance (R_p).

Sodium benzoate converts to benzoic acid when used in acidic mixtures. Benzoic acid has good anti-microbial features, but does not dissolve well in water, whereas sodium benzoate dissolves very well in water. It is also used as a corrosion inhibitor in automotive anti-freeze products.

1.2 UMT Research Vessel and Research Motivation

UMT Research Vessel was built to fulfil the university's research and teaching needs. The vessel is being employed to support Institute of Oceonography (INOS) research activities. The latest task is surveying South China Sea for submarine routes. The vessel also serves for students activities of Maritime Technology Department, Nautical Science and Transportation Department, Marine Science Department, and Maritime Management Department.

The vessel is 35m long and made of aluminum as shown in Figure 1. It is powered by 634kw engine and its gross tonnage is 291. It has several small compartments to serve as ballast tank and to keep marine samples. The compartments are also made of aluminum (Si (0.20%), Fe (0.35%), Cu (0.10%), Mn (0.10%), Mg (0.45%), Cr (0.1   0%), Zn (0.10%), Ti (0.10%) and Al (reminder) by weight).

Figure 1. 35 m long UMT Research Vessel.

Beside this RV, UMT has nine other boats or small vessels. Aboard these vessels, there are quite expensive equipments. Since they are heavily used for teaching and research, they are always exposed to sea environment. Significant corrosion was observed in sampling tanks which normally contains sea products and palm oils. Figure 2 shows one of the sampling ballast tanks which was heavily corroded. This phenomenon attracts the researchers to study marine corrosion.

Figure 2. Actual corrosion on ballast tank.

2. METHODOLOGY

2. 1 Materials

In this laboratory scale study, the material employed was AA6063 (25 x 25 x 1.5 mm coupons). The actual seawater was used as the test solution. The inhibitor used was sodium benzoate, NaBz ($1g/dm^3$ concentration).

Several studies have been carried out on corrosion inhibitor; many of them concluded that corrosion was uniform with sodium benzoate. Benzoic acid and its sodium salt (sodium benzoate) are the most common, safe, food preservatives and antimicrobial agents. Benzoic acid and sodium

benzoate are classified in the United States as Generally Recognized as Safe (GRAS) and their use in food is permitted up to a maximum level of 0.1%. Commercial availability and low cost of benzoic acid and sodium benzoate make them attractive candidates to be incorporated into coatings as environmentally benign alternatives (Al-Juhni and Newby [2]).

2.2 Methods

Sophisticated corrosion inhibitor test methods, typically designed to reproduce the most extreme conditions in a system, have been employed to improve inhibitor capabilities. Research of uniform corrosion is the most widespread application of electrochemical measurements both in the laboratory and industry. The widespread use of these electrochemical methods comes with limitation (Yagan et al. [14]).

2.3 Electrochemical Impedance Spectroscopy (EIS)

Circuit model or circuit description code and initial circuit parameters were assumed and input by the operator based on the shape of the EIS spectrum. The program then fits the best frequency response of the given EIS spectrum, to obtain fitting parameters. The quality of the fitting was judged by how well the fitting curve overlaps the original spectrum. The fitted EIS data was used to obtain a set of parameters which can be correlated with the coating condition and the corrosion of the steel substrate.

2.4. Electrochemical Analysis Process

The preparation of working electrode before measurements is the same as described before (Rosliza and Wan Nik [11]). Electrochemical potentiodynamic reactivation (EPR) is probably the most commonly used polarization testing method for measuring corrosion resistance and is used for a wide variety of functions. Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. This technique uses a potentiodynamic scan over a range of potentials from passive to active (called reactivation) to measure the degree of sensitization of stainless steels.

All electrochemical measurements were accomplished with Autolab frequency response analyzer (FRA) coupled to an Autolab potentiostat connected to a computer. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -250 mV to +250 mV with the scanning rate of 5 mVs^{-1}. Impedance measurements were conducted over a frequency range of 10^4 Hz to 10^{-1} Hz. The data were presented as Nyquist plots.

3. RESULTS

Figure 3 illustrates the weight loss of AA6063 alloys in seawater with static condition with and without NaBz as inhibitors. Figure 4 presents the corrosion rate versus the immersion time of the aluminium alloy samples in seawater with and without inhibitor. Figure 5 represents the potentiodynamic polarization curves of AA6063 in seawater in the absence and the presence of NaBz.
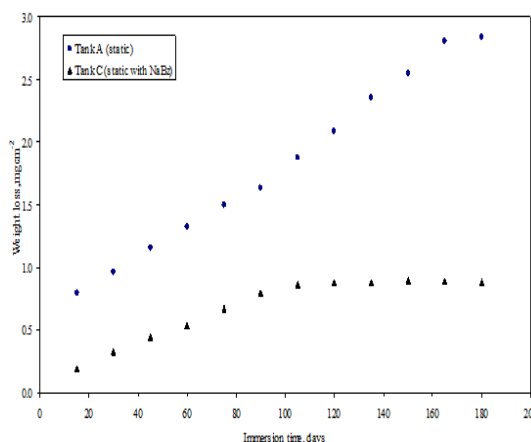

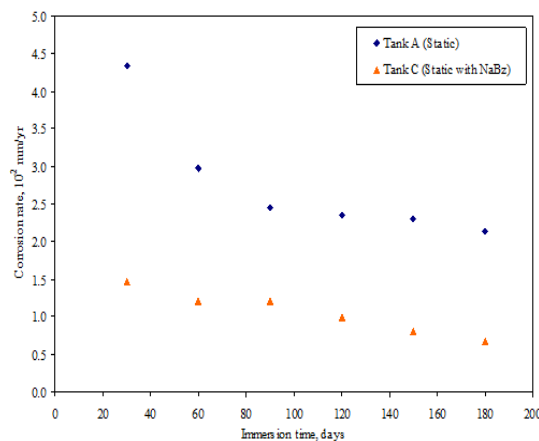Figure 3. Weight losses versus immersion time of AA6063.

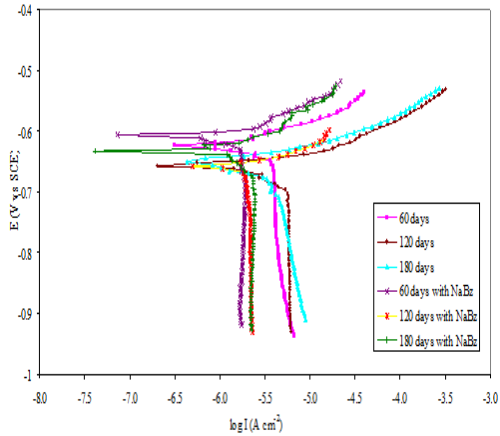Figure 4. Corrosion rate versus immersion time of AA6063.

Figure 5. Potentiodynamic polarization curves for AA6063.

The values for the corrosion potentials and corrosion current densities were estimated from the intersection of the anodic and cathodic Tafel lines. The corresponding corrosion potentials (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slopes (b_a) & cathodic Tafel slopes (b_c) are listed in Table 1. Table 2 displays the results of the values of the IE (%) from the weight loss and electrochemical tests.

Table 1. The electrochemical parameters: E_{corr}, i_{corr}, b_a, b_c and R_p of AA6063 in seawater.

Condition	NaBz	Days	Potentiodynamic polarization		Linear polarization
			E_{corr} (mV)	i_{corr} ($\Box$A cm^{-2})	R_p (k$\Box\Box$ cm cm^2)
Static	Absence	30	-658	0.04	206.3
		60	-669	0.17	112.3
		90	-659	0.49	46.6
		120	-669	0.79	18.2
		150	-668	1.54	9.2
		180	-656	2.18	1.1
	Presence	30	-708	0.01	650.9
		60	-664	0.06	296.0
		90	-624	0.23	98.0
		120	-670	0.33	43.8
		150	-687	0.53	26.3
		180	-689	0.66	3.7
		180	-629	1.86	1.0

Table 2. Values of IE (%) for AA6063 samples in seawater.

Condition	Days	IE (%)		
		Weight loss	PP	EIS
Static	30	66.1	72.0	68.82
	60	59.3	63.8	63.58
	90	51.0	53.1	54.37
	120	57.8	58.9	57.08
	150	64.7	65.5	63.12
	180	68.4	69.7	66.16
	180	40.9	50.1	49.11

4. DISCUSSION

Figure 2 shows the severity of one of our vessel ballast tank. It was the result of almost 20 years of seawater corrosion. This real life corrosion is very complicated to be simulated in laboratory environment.

4.1 Weight Loss Measurements

Results from Figure 3 show that the weight losses of AA6063 for all samples increase with the immersion time. The corrosion rate tends to be increased by decreasing temperature, pH, and flow velocity and by increasing dissolved oxygen (Hollingsworth and Hunsicker [7]). Values of salinity and pH measured during the immersion test are stable (in the range of nature seawater). Baorong et al. [4] reported that there was no obvious effect when the seawater salinity was varied from 30% to10%.

Clear differences can be noted between the samples exposed to seawater containing NaBz as compared to that immersed in the absence of the inhibitor. The test without inhibitor addition had the higher weight loss. There was a reduction in weight loss; hence reduced the corrosion rate with the introduction of NaBz as an inhibitor into the seawater for both cases in static condition.

The obtained results from Figure 4 demonstrate that the test without inhibitor addition in static condition had the higher corrosion rate. The results indicated that introduction of NaBz obviously minimize the rate of corrosion and abridged aluminium dissolution in seawater. Therefore this inhibitor can be considered as efficient inhibitor for AA6063 in seawater.

4.2. Potentiodynamic Polarization Studies

The changes observed in the polarization curves after addition of the inhibitor are usually used as criteria to classify inhibitors as cathodic, anodic or mixed (Bethencourt et al. [5]). From Figure 5, it can be seen that the anodic and cathodic current densities obtained in the presence of inhibitor are lower than as compared to that of in the absence of inhibitor. The corrosion potential (E_{corr}) values in the presence of inhibitor are shifted to negative direction and leftward displacement in the cathodic branch of the curves. According to Trabanelli et al. [13], these are the typical features of cathodic inhibitors, this being in agreement with the results obtained for other aluminium alloys.

EIS research has proved that EIS is a powerful and accurate method for measuring corrosion rates. In order to access the charge transfer resistance and polarization resistance that is proportional to the

corrosion rate at the monitored interface, EIS results is interpreted by model of the interface. Advantage of EIS techniques is the possibility of using very small amplitude signals without disturbing the properties being measured. In EIS measurement, a small amplitude signal, usually a voltage between 5 to 50 mV is applied to a specimen over frequency range of 0.001 Hz to 100,000 Hz.

The EIS instrument records the real resistance and imaginary capacitance components of the impedance response of the system. Equivalent circuits that describe electrochemical of a freely corroding interface at kinetic equilibrium are (Al-Juhni and Newby [2], Yagan et al. [14]):

- Relaxation time constant with extended diffusion.
- Impedance of pitting processes.
- RC representation of an electrochemical interface.

The results display in Table 1 show that the values of corrosion current density (i_{corr}) for all samples increase with the immersion time. The change in E_{corr} is assumed to be related to the growth of a passive layer at the surface of electrode (Rosalbino et al. [9]). The rate of cathodic reaction controls the rate of the corrosion process (as the cathodic over voltage is much greater than the anodic one). The corrosion current decreases obviously after sodium benzoate is added in test solution. It is clear that the presence of inhibitor causes markedly decrease in the corrosion rate. The corrosion resistance of the investigated material is remarkably higher in the benzoate containing than benzoate free solution (Bethencourt, et al. [5]).

4.3 Electrochemical Impedance Spectroscopy

The shape of the obtained Nyquist plots shows single capacitive semicircles, showing that the corrosion process was mainly charge-transfer controlled (El-Etre, [6] and Trabanelli et al. [13]). The general shape of the curves is very similar for all the samples and this is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the immersion time or to the inhibitor addition (Reis et al. [8]). Inspection of the data reveals that the impedance spectra consists of a large capacitive loop at high frequencies corresponding to the relaxation processes in the oxide film covering the electrode surface (Abd El Rahim et al. [1]). In all cases, single capacitive loops are observed which sizes decrease with the exposure time.

The equivalent circuit fitting for these experimental data was a Randles circuit. The Randles equivalent circuit is one of the simplest and most common circuit models of electrochemical

impedance. It includes a solution resistance, R_s in series to a parallel combination of resistor, R_{ct}, representing the charge transfer (corrosion) resistance and a double layer capacitor, C_{dl}, representing the electrode capacitance (Badawy et al. [3]).

After 180 days immersion time, the charge transfer resistance, R_{ct} for the aluminium alloy decreased to the likely formation (or thickening) of a corrosion product layer on the electrode. The R_{ct} values were higher for AA6063 after addition of inhibitor at all the immersion time, indicating that NaBz is inhibiting the corrosion rate. It can be concluded that NaBz is an effective inhibitor for the aluminium alloy.

4.4. Inhibition Efficiency and Adsorption Isotherm

The inhibitor such as benzoate group adsorbs on aluminium alloy. As a result a thin film is formed on the aluminium alloy to retard the corrosion. Thus, in this case, sodium benzoate worked as filming inhibitor to control the corrosion rate. Instead of reacting with or removing an active corrosive species, filming inhibitors function by strong adsorption and decrease the attack by creating a barrier between the metal and their environment (Al-Juhni and Newby [2]).

The values of the IE (%) from the weight loss and electrochemical tests were calculated using the same equations as previously report (Rosliza and Wan Nik, [12]). The values of IE (%) for the samples at different immersion time are given in Table 2 and the trends were similar for all three different types of measurements.

5. CONCLUSION

The corrosion studies of AA6063 aluminium alloy have been carried out at room temperature using seawater. The results obtained lead to the conclusion that NaBz is an effective corrosion inhibitor of AA6063 in seawater. The potentiodynamic polarization curves suggested a cathodic character for the inhibition process in seawater. EIS measurements clarified that the corrosion process was mainly charge-transfer controlled and no change in the corrosion mechanism occurred either due to the immersion time or the inhibitor addition to seawater.

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REFERENCES

[1] Abd El Rahim, SS., Hassan, HH., Amin, MA., "The corrosion inhibition study of sodium dodecyl sulphonate to aluminum and its alloy in 1.0 M HCl solution." *Mater Chem Phys*, Vol. 78, pp. 337–348, Elsevier (2003).

[2] Al-Juhni, AA., Newby, BZ., "Incorpora-tion of benzoic acid and sodium benzoate into silicone coatings and subsequent leaching of the compound from the incorporated coatings.," *Prog Org Coatings*, Vol. 56, pp. 135–145, Elsevier (2006)

[3] Badawy, WA., Al-Kharafi, FM., El-Azab, AS., "Electrochemical behaviour and corrosion inhibition of Al, Al-6061 and Al-Cu in neutral aqueous solutions," *Corros Sci*, Vol. 41, pp. 709–727, Elsevier (1999)

[4] Baorong, H., Jinglei, Z., Yanxu, L., Fangying, Y., "Study on effect of seawater saliniyu on electrochemical performance of Al anodes," Department of Marine Corrosion, Institute of Oceanology, Chinese Academy of Sciences, China (2001).

[5] Bethencourt, M., Botana, FJ., Cauqui, MA., Marcos, M., Rodriguez, MA., "Protection against corrosion in marine environments of AA5083 Al-Mg alloy by lanthanide chlorides," *Alloys Compounds*, Vol. 250, pp. 455–460, Elsevier (1997).

[6] El-Etre, AY., "Inhibition of aluminum corrosion using *Opuntia* extract," *Corros Sci*, Vol. 45, pp. 2485–2495, Elsevier (2003).

[7] Hollingsworth, EH., Hunsicker, HY., "Corrosion of aluminum and aluminum alloys," *ASM Metals Handbook*, Vol. 13, pp. 582–609 (1987).

[8] Reis, FM., de Melo, HG., Costa, I., "EIS investigation on Al 5052 alloy surface preparation for self-assembling monolayer," *Electrochimica Acta*, Vol. 51, pp. 1780–1788, Elsevier (2006).

[9] Rosalbino, F., Angelini, E., De Negri, S., Saccone, A., Delfino, S., "Electrochemical behavior assessment of novel Mg-rich Mg-Al-RE alloys (RE=Ce, Er)," *Intermetallics*, Vol. 14, pp. 1487–1492, Elsevier (2006).

[10] Rosliza, R., Wan Nik, WB., "The effect of inhibitor on the corrosion of aluminum alloys in acidic solutions," *Mater Chem Phys*, Vol. 107, pp. 281–288, Elsevier (2008a).

[11] Rosliza, R., Wan Nik, WB., "Electrochemical properties and corrosion inhibition of AA6061 in tropical seawater," *Colloids Surf A*, Vol. 312, pp. 185–189, Elsevier (2008b)

[12] Rosliza, R., Wan Nik, WB., "Improvement of corrosion resistance of AA6061 alloy by tapioca starch in seawter," *Current Applied Physics*, Vol. 10, pp. 221–229, Elsevier(2010).

[13] Trabanelli, G., Monticelli, C., Grassi, V., Frignani, A., "Electrochemical study on inhibitors of rebar corrosion in carbonated concrete," *Cement Concrete Research*, Vol. 35, pp. 1804–1813, Elsevier (2005).

[14] Yagan, A., Pekmez, NO., Yildiz, A., "Corrosion inhibition by poly (*N*-ethylaniline) coatings of mild steel in aqueous acidic solutions," *Prog Org Coatings*, Vol. 57, pp. 314–318, Elsevier (2006).