BIOSCIENCES BIOTECHNOLOGY RESEARCH ASIA, April 2015. Vol. **12**(1), 71-76

Corrosion Performance of Coating Thickness in Marine Environment

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DOI: http://dx.doi.org/10.13005/bbra/1637

(Received: 20 January 2015; accepted: 01 March 2015)

Traditionally, zinc has been used as metallic material to protect steel against atmospheric corrosion. The coatings are used for corrosion protection in a variety of industrial applications. This is due to its ability to provide cathodic protection to steel in all types of natural atmospheres. In the effort of determining the optimum coating thickness, a comparative study of the corrosion on mild steel coated by different thickness of zinc in marine environment was carried out. This paper presents the corrosion study of two marine environment which are immersion in seawater and also in salt spray splash environment. The aim of this study is to compare by experiment the corrosion rate of mild steel coated by different thickness of zinc under salt spray and also immersion. The corrosion measurement test was performed by weight loss measurement, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The morphological study on the surface degradation of the coated steel was performed by using scanning electron microscopy (SEM). The investigation on corrosion rate for the salt spray test shows higher loss percentage compared to seawater immersion. The bare mild steel recorded the highest corrosion rate compared to the other coated mild steel in both environments.

Key words: Marine environment, Mild steel, Potentiodynamic polarization, SEM, zinc coating.

The word corrosion is as old as the earth but it has been known by different names. In general, corrosion can be described as rust and can be seen as the destruction of a material under undesirable phenomena which destroys the beauty of objects and shortens their life. Generally, corrosion is an electrochemical process. When oxygen reacts chemically with steel, oxidation or rusting process occurred. While the rusting process occurs, steel is consumed during the corrosion reaction, where it converts iron to the corrosion products. The presence of chloride ion in the sea water is one of the factors that accelerate the rate of the corrosion to occur. Furthermore, for immersion environments, influences on corrosion can include chemical factors such as salinity, oxygen content, pH and presence of pollutants, physical factors such as temperature and pressure (Qian, et al. 2013).

In many industries, thereis a need to use constructional materials safely, but at the same time cost-effectively, where the safety is the primary consideration (Rahim, et al.2007). The wastage of metals due to corrosion is one of the most serious engineering problems today and is of great economic concern(Hollingshead and Hanham

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1984).

Corrosion is the most widespread form of metal deterioration, because most metallic structures and equipment installations are exposed to natural corrosive environments(Gulec, et al. 2011). Mild steel, or in other words is carbon steel, are widely used in maritime industry due to the least expensive, most versatile and widely used in engineering material which has found extensive application in various industries.

Carbon steel is a remarkably cheap material, with good tensile strength (350 – 850 N/mm^2 in normalised plain carbon steels), and easy to weld using gas, arc or resistance welding (Otunniyi and Oloruntoba 2012).In addition, it is having good mechanical properties. Although easy, low-cost manufacture makes their use attractive, their resistance to atmospheric corrosion is very low in most environments and progressive deterioration of their structure leads to rust formation and consequent loss of some of their mechanical properties(Rincon, et al. 2009).Pitting is a form of corrosion observed in some metals where corrosion is localized to small areas of degradation. It can lead to catastrophic consequences in marine applications. Pitting is thought to be the most common type of localized (Caines, et al. 2013)

There are several ways on how to overcome corrosion. The possible ways of controlling corrosion are application of coatings, linings, metal cladding, corrosion inhibitors and alloying. Among these, application of suitable coatings appears to be a promising method of corrosion control in terms of cost effectiveness and service (Garuppa and Malakondaiah, 2005). Metallic coatings are one of the main ways of protecting steel against corrosion (Panossian, et al. 2005). In coating applications, zinc containing paint is widely used due to their high corrosion protection performance.

From previous researches, several researchers examined the corrosion protection properties of zinc- containing paints and discovered the cathodic protection mechanism of zinc-containing paints on metal (Shon 2010). Zinc-rich layer is used as a single coat or as a component of paint system. Coating system consisting of zinc-rich primer and topcoat offer decorative and barrier as well as anti-corrosive protection to the steel substrate(Schaefer and Miszczyk, 2013). Initially, when paint that contains a thin layer is applied in any surface, it starts to absorb oxygen from air that makes a solvent resistant elastic coat (Kemalov, et al. 2014).

Spray application is widely used in industry and it also gives many advantages. The advantages of this method is about the speed of application, it can control of film thickness and allow the use of fast drying coatings (Coating application guide 2010). Furthermore, it can be uniform finished and lastly can be installed as an automatic process. The basic principle of spray application is to atomize the paint into a fine spray and to direct the spray onto the object to be coated.

Corrosion protection measures include paint coatings and sacrificial anode systems for immersed areas. Ships are exposed to a range of corrosion environments and as a result the patterns of corrosion vary widely. For immersion environments, influences on corrosion include chemical factors such as oxygen content and pH; physical factors such as temperature and pressure; and biological factors such as bacteria and biomass (Gudze and Melchers, 2008).

Methodology

Specimen preparation

Test material selected for study is mild steel. Mild steel used was SS400, gred A36. Mild steel samples with a dimension of a rectangular shape of 25x25x3 mm were polished by using copper brushed, so that the corroded materials which remain on the metal can be polished as well. The next step,the specimen was immersed in thinner solution to clean and free the metal from the oil. The other purpose of immersing the samples into the thinner is to increase the adhesion of paint to the samples surfaces. Lastly, the samples were stored in the desiccators. The environment chosen is in submerged and splash (salt spray) zone.

Coating and scratch process

For this study, the coating method used was compressed air spraying. Before spraying, the paint formulation was identified. For every 100 ml of zinc rich primer, 150 ml of thinner and 30 ml of hardener were used to obtain the suitable mixture. The mixture was then stirred for about five to seven minutes to ensure the paint was well mixed. Next, the samples were subjected to spraying process. The coating thickness required in this study is 50 µm, 150 µm and 250 µm. Next, the samples were dried in vacuum oven until the paint is fully dried. A scratch hardness was conducted after the coating of paint was dried. This process was conducted by using Scratch, Adhesion and Mar (SAM) tester.

Immersion preparation

The immersion preparation was done in the laboratory. The aquarium was filled with seawater until half full level, approximately 10 to 11 liter. Basically, from our experience, the level of seawater does not affect the corrosion results at all, as long as the metal is completely immersed. Next is the labeling process. The labeling was done on the catguts where the metals were tied. The tying of catguts to the plastic net must be done in four lines to differentiate between 15th days, 30th days, 45thdays and finally 60th days.

Additional device

In this study, the wave motor was used. The purpose of using this device is to give waves and as a simulation like open sea. The wave motor was located at the center of the aquarium so that the amount of waves produced is equally distributed to the whole aquarium.

Salt spray preparation

For salt spray preparation, all specimen used was tied to the special hanger inside the salt spray chamber. The water container of salt spray was filled with seawater by using filter to prevent the sediments from entering to the container. Next, the salt spray chamber and the compressor were turned on and the water entered the chamber via tube and simulatedareal splash zone.

Corrosion measurement test

Weight loss measurement

The initial weight (w_i) was taken beforetestedin environments of immersion and salt spray zone. For final weight, the samples were soaked in a beaker in nitric acid solution. The purpose of using nitric acid is to remove the rusting that was produced at metal surfaces. Next, the samples were transferred into distilled water solutions about 2-3 minutes to rinse the metal from nitric acid. Lastly, the samples were dried in room temperature and final weight was taken. The readings were recorded in a table form.

Electrochemical measurement

For electrochemical measurement, the Autolab software was used. Two measurements which are General Purpose Electrochemical System (GPES) and Frequency Response Analyzer (FRA) were used to analyze the data. The scanning rate of 0.0101Vs^{-1} was set and for the potentiodynamic polarization (PP), the exposed area of the metal was 2.3395 cm^2. From the graph, the value of corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel Slope (b_a), cathodicTafel Slope (b_c) from the intersection of the linear anodic and cathodic branches of the PC as Tafel plots were obtained.

Scanning electron microscopy (SEM)

The surface morphology of mild steel can be observed by using SEM method. By performing SEM, the differences of surface content between bare mild steel and different coating thickness of mild steel can be identified. For this test, the electrons interact with electrons in the sample, producing various signals that can be detected and contain information about the sample's surface topography and composition.

RESULTS AND DISCUSSIONS

Corrosion measurement test

Weight loss measurement

The result obtained for weight loss test after every 15 days with the total period of 60 days. The value of corrosion rate was obtained from weight loss measurements of different coating thickness in both seawater immersion and salt spray zone. Figure 1 shows the graph of weight loss percentage (%) versus immersion time (days) for seawater immersion, while Figure 2 shows the graph of loss percentage (%) versus immersion time (days) for salt spray zone. Figure 1 shows that when the coating thickness increases, the corrosion rate decreases. The weight loss percentage at salt spray zone is higher compare to seawater immersion (Figure 2), which means that the corrosion rate at salt spray zone is higher.

Potentiodynamic polarization scan

From Figures 3 and 4, the results show that the values of corrosion potential, E_{corr} move towards electropositive region as the coating thickness increased. The valueof$E_{corr}$for bare mild steel, is obviously situated at more electronegative region which is about -0.7V, compared to the coated mild steel which is somewhere around -0.57V to -0.60V for seawater immersion. For salt spray test, values of E_{corr} for 150 µm and 250 µm show the small differences which are around -0.6V to -0.62V. The higher value of $E_{corr,}$ indicates lower corrosion rate.

Table 1 shows seawater immersion test parameters while Table 2 shows salt spray test parameters. The value of corrosion rate decreases as the coating thickness is increased. When the

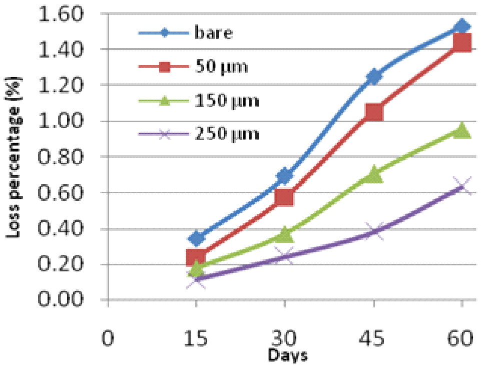


Fig. 1. Weight loss percentage vs days for seawater immersion

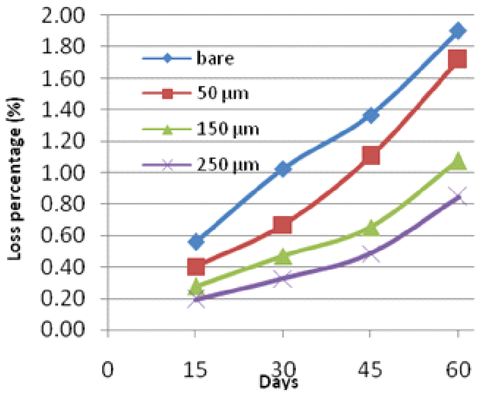


Fig. 2. Weight loss percentage vs days for salt spray zone

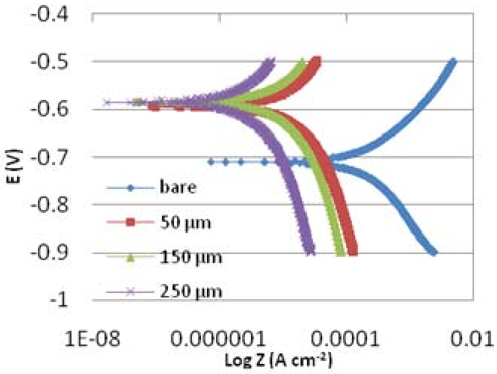


Fig. 3. Polarization curves of mild steel in seawater immersion

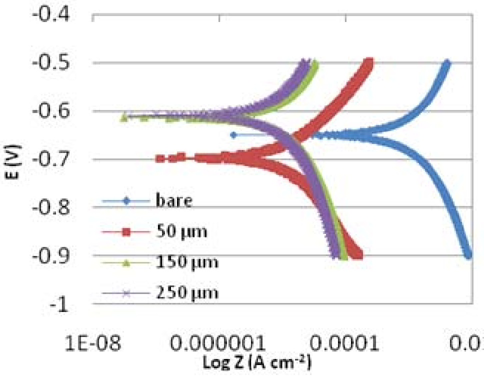


Fig. 4. Polarization curves of mild steel in salt spray zone

Table 1. Corrosion parameters of mild steel in seawater immersion

Thickness	*ba*(V/dec)	*bc*(V/dec)	$E_{corr,}$Calc (V)	I_{corr}(A)	Corrosion rate (mm/year)
Bare	0.0022	0.005491	-0.71134	3.99E-06	0.019808
50 µm	0.0041	0.004735	-0.5948	1.98E-07	0.000984
150 µm	0.00 22	0.004188	-0.58454	1.09E-07	0.000544
250 µm	0.0032	0.005439	-0.58634	4.97E-08	0.000247

Table 2. Corrosion parameters of mild steel in salt spray zone

Thickness	*ba* (V/dec)	*bc*(V/dec)	$E_{corr,}$Calc (V)	I_{corr} (A)	Corrosion rate (mm/year)
Bare	0.00495	0.00523	-0.6497	2.03E-05	0.10102
50 µm	0.0071	0.00568	-0.6974	3.71E-07	0.00184
150 µm	0.00418	0.00513	-0.6139	2.08E-07	0.00103
250 µm	0.00452	0.00414	-0.6095	1.35E-07	0.00067

coating thickness increases the value of corrosion current density I_{corr} decreases.

Electrochemical impedance spectroscopy (EIS)

For this test, a Nyquist plot was used to analyze the data. Figure 5 shows the data analyzed from seawater immersion, and Figure 6 shows for salt spray zone. Increasing in coating thickness gives results to higher semicircles formed. From both graphs, 250 µm thickness sample shows the highest semicircle compared to other thickness. R_s of 250 µm started far from 0 values due to the far distance between reference electrode and working electrode during the analysis work.

Higher value of charge transfer resistance, R_{ct} and lower value of double layer capacitance, C_{dl} indicates that the corrosion rate is low. The value of R_{ct} and C_{dl} for both seawater immersion and salt spray zone are illustrated in Table 3 and Table 4 respectively.

Scanning electron microscopy (SEM)

For SEM, the surface morphology was observed and analyzed for mild steel before and after the test. The surface morphology for coated steel is almost the same for all thickness, which shows the content of paint.

From Figure 7(i), it shows the clear surface of bare mild steel before tested without any morphology. Next, Figure 7(ii) indicates the surface morphology of coated mild steel before test. The bubble formed is from the uneven spraying of paint during the coating process. After the immersion period of 60 days, morphology for bare mild steel is as shown in Figure 7(iii). There are many cracks produced since the metal was not protected by any material. Furthermore, one of the properties of mild steel is that it can easily crack when exposed to environments especially marine environments. The last figure which is Figure 7(iv) shows the morphology for coated mild steel after the test. From this study, the morphology of coated mild steel after the test is similar for both seawater immersion and salt spray test. From Figure 7(iv), it can be clearly seen that many round shape particles are produced. Generally, the particle showsisthe salt content at the surface of mild steel.

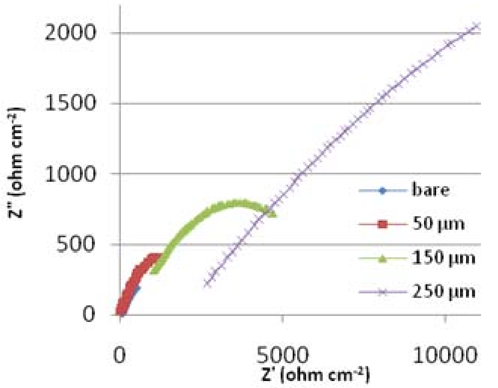


Fig. 5. Nyquist plots of mild steel immersed in seawater

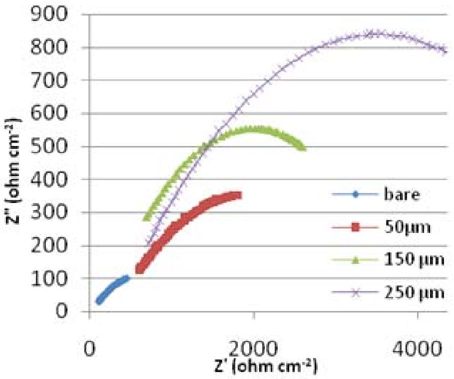
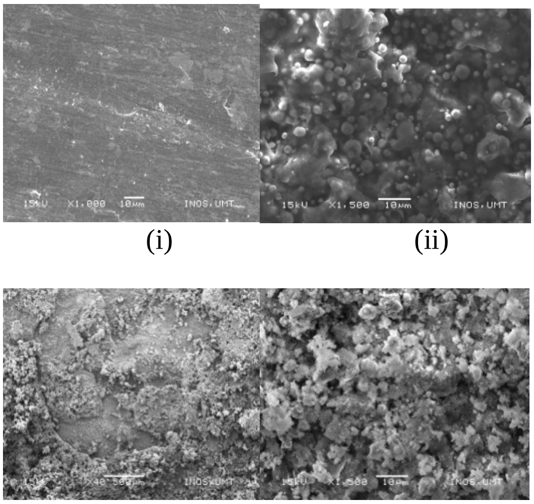


Fig. 6. Nyquistplots of mild steel in salt spray zone



(i) (ii)

(iii) (iv)

Fig. 7. SEM micrograph of the surface of mild steel before and after the test.

CONCLUSIONS

Based on the previous research, the use of zinc rich primer as a coating material for steel is widely used due to their high corrosion protection performance. Moreover, when referring to galvanic series, zinc is situated in less noble category and also one of the reasons why zinc is selected frequently. From the study, as the coating thickness increase, the corrosion rate decreases. These results can be seenfrom all test conducted. For weight loss, the percentage loss for bare mild steel is higher compare to the coated mild steel. The graphs also clearly shows that the percentage loss for salt spray test is higher compare to seawater immersion. For potentiodynamic polarization and electrochemical impedance spectroscopy, the value of polarization resistance, $R_p$increases as the coating thickness increases. Highest value of R_p gives a stronger protection towards the metal from corrodes. When R_p is high, double layer capacitance, C_{dl}decreases as thin film formed on the surface decrease. For overall conclusion, increasing in coating thickness will decrease the corrosion rate of mild steel. Lastly by comparing two different marine environments, salt spray showing the higher corrosion rate of mild steel compared to seawater immersion.

ACKNOWLDGEMENTS

The authors would like to express their deepest gratitude for the fund and scholarship provided by Ministry of Education, Malaysia (FRGS: Vot 59210, and Vot 59283). The author greatly acknowledge, Muhammad Amirul Ariffin Bin Muhammad Alim for his direct contribution in this study.

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