



THE DEVELOPMENT OF PORTABLE IN-SITU OPEN CIRCUIT POTENTIAL TEST CELL

This report is submitted in accordance with requirement of the Universiti Teknikal
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(Engineering Materials) (Hons.)

by

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Date : 20 June 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

.....
(Dr. Muhammad Zaimi bin Zainal Abidin)

ABSTRAK

Ujian lapisan cat adalah sangat penting untuk menentukan lapisan kecacatan dan untuk mencegah kakisan serta degradasi. Terdapat banyak kaedah “Non-destructive” untuk menentukan kecacatan lapisan seperti ujian ultrasonik, ujian magnet dan ujian radiografi. kaedah pengukuran elektrokimia adalah satu kaedah yang baik dan boleh mengesan rintangan lapisan, liang kecil dan calar. Walaubagaimanapun, kaedah pengukuran elektrokimia biasanya digunakan di dalam makmal dan memusnahkan sampel. Oleh itu, tujuan kajian ini adalah untuk mereka bentuk siasatan elektrokimia untuk mengukur potensi permukaan pelbagai kecacatan lapisan. Sampel kajian terdiri daripada keluli karbon ASTM A516 disalut dengan cat kaca epoksi dari Jotun sehingga tebal 1 mm. Saiz grid adalah 5×10 persegi dengan keluasan 1 cm^2 telah dibuat pada lapisan permukaan keluli karbon. Elektrod prototaip yang digunakan adalah mata pensil grafit dan Cu / CuSO₄ (tepu) sebagai elektrod kaunter dan elektrod rujukan. Potensi kecacatan lapisan diatas permukaan diukur menggunakan kaedah “open circuit potential.” Hasil dapatan daripada pengukuran potensi setiap permukaan grid kemudiannya diubah kepada imej tomografi. Prototaip sebenar kemudiannya direka dengan menggunakan perisian SolidWorks dan kemudian dicetak dalam bentuk 3D menggunakan pencetak prototaip pantas. “Pilot test” telah dilakukan terhadap prototaip elektrokimia untuk menguji kebolehkerjaannya. Pengukuran potensi permukaan boleh diperhatikan melalui warna kontur yang berbeza. Hasil dapatan menunjukkan kecacatan lapisan yang kurang dalam menunjukkan potensi permukaan lebih rendah berbanding dengan kecacatan yang lebih dalam. Potensi kakisan pelbagai kecacatan lapisan ditentukan dan disahkan. Kemudian, siasatan kebolehkerjaan prototaip elektrokimia sebenar telah diuji di makmal dan ia mengesahkan bahawa prototaip elektrokimia boleh digunakan.

ABSTRACT

Coating testing is very crucial to determine coating defect and to prevent corrosion as well as degradation. There are many non-destructive methods to determine coating defects such as ultrasonic testing, magnetic testing and radiographic testing. Electrochemical measurement method is a powerful method that can detect coating resistances, pinholes and scratches. However, the electrochemical measurement method is usually used in the laboratory and requires the destruction of samples. Hence, the aim of this study is to design an electrochemical probe to measure surface potential of various coating defects. A sample of carbon steel ASTM A516 is coated with glass flake epoxy paint from Jotun until 1 mm thick. The coated carbon steel surface is made into square grid of 5×10 with area of 1 cm^2 per square. Using prototype electrode made from pencil graphite and Cu/CuSO_4 (saturated) as counter and reference electrodes respectively, the surface potential of the coating defect grid is measured using open circuit potential measurement. The surface potential measurement results of each grid are then transformed into tomography image. The results are then verified with the defects and its reproducibility. The final prototype is then designed using SolidWorks software and then 3D printed using rapid prototype printer. The pilot test electrochemical probe prototype was tested to observe the workability of the electrochemical probe. The surface potential measurement can be observed through the different contour colours. From the results, the coating defect with less deep defect shows lower surface potential compare to deeper defect. The corrosion potential of various coating defects was determined and verified. Then, the actual electrochemical probe prototype workability was tested in laboratory and it resulted that the electrochemical probe is workable.

DEDICATION

Only

my beloved father, Abd Latif bin Omar

my beloved mother, Fatimah binti Hashim

my adored brother, Muhammad Dzul Farhan bin Abd Latif

for giving me moral support, money, cooperation, encouragement and also understandings

Thank You So Much

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
ASTM	-	American Society for Testing and Materials
ISO	-	International Standards Organization
NACE	-	National Association Corrosion Engineering
OCP	-	Open Circuit Potential
SKP	-	Scanning Kelvin Probe
SKPFM	-	Scanning Kelvin Probe Force Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Corrosion of metal and alloys causes loss of billions USD per year in term of maintenance cost. Coating is one of the cheapest methods to protect metallic surface from corrosion by providing a chemical resistant, non-reactive and good appearance to the metallic surface. Nevertheless, coating defect before commission and during service is one of the main reasons of corrosion. There are many coating defect detection method such as non-destructive method, surface detection method and electrochemical measurement method. Electrochemical measurement method is one of the most powerful methods to detect coating defect by measuring surface potential as well as resistance. However, most of the electrochemical measurement is done in a laboratory and requires samples destruction. The surface where the electrochemical reduction takes place is known as the outer-Helmholtz layer. At this surface layer, the positively charged layer containing cations is closest to negatively charged surface layer. In-situ methods are those where a surface is probed by one or several techniques while immersed in solution and under potential control(John et al., 2002). Open circuit potential (OCP) variations can be measured from the difference voltage results between immersed metal in electrolyte solution and a good reference electrode (Sahrani et al., 2008). The OCP can be measured using classical three electrode cell with working electrode, counter electrode and reference electrode. The surface OCP also represent as corrosion potential where anodic reaction and cathodic reaction current density approach zero.

Hence, it is possible to determine the surface of structure's corrosion behaviour by observing the OCP changes versus time. Nevertheless, the OCP measurement is usually done in a laboratory, thus, it cannot be used for in-situ measurement in a chemical plant for example.

In this study, the surface OCP was measured using a portable electrochemical electrode cell designed for in-situ measurement. The portable electrochemical probe prototype was made for electrochemical testing and the OCP measurement is done on a surface of coated carbon steel with surface coating defects in grids to determine its feasibility. The probe composed of Cu/CuSO₄ (saturated) and graphite as reference and counter electrode respectively. The coated metal surface was used as working electrode with several defects in the grids. The electrolyte for the testing is 3.5wt% NaCl aqueous solution. Each square of the grid was measured and made into tomographic diagram. The actual design of the probe was designed using Solidworks software. The final design will be formed using 3D printer.

1.2 Problem Statement

There are several methods of surface coating evaluation during online operation such as using Eddy current technique and some custom made ultrasonic testing. However, these methods are limited to evaluate thickness, pinhole, and defect without knowing its possibility of electrolyte intrusion. Hence, the defect of coating may lead to undercoating corrosion. The corrosion also can be inspected by using visual inspection, but very limited and depended on inspector personnel experience. Electrochemical measurement technique can be used to detect very small difference of surface potential that related to corrosion reaction such as open circuit potential, linear scanning voltammetry and electrochemical impedance spectroscopy. Nevertheless, these methods are suitable only for laboratory scale not in-situ measurement. Therefore, the development of portable in-situ open circuit potential test cell is to overcome the difficulties in the corrosion testing by using the in-situ concept using open circuit potential measurement method. The development of the probe includes verifying the surface potential measurement theory using the electrochemical probe on various kinds of coating defect and designing the probe using SolidWorks software.

1.3 Objectives

The objectives of this study are:

1. To design the electrochemical probe using SolidWorks software
2. To verify the surface potential measurement theory on various coating defect using electrochemical probe

1.4 Scope of study

A prototype electrochemical probe is made using recycled materials with Cu/CuSO₄ (saturated) and graphite as reference and counter electrode respectively. The feasibility study on OCP measurement is done on the metal or coated surface as working electrode. The sample surface is in form of grids with several defects on it. The result of the OCP measurement is made into tomographic diagram. The SolidWorks 2013 software is used to design the actual probe and to be formed using 3D printer.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion

As indicated by ISO 8044:2015, corrosion is physicochemical cooperation between a metal and its surroundings that outcomes in changes in the properties of the metal, and prompt to huge weakness of the capacity of the metal, nature, or the specialized framework, of which these shape a section. Corrosion is the procedure of metal coming back to the material's thermodynamic state there is development of oxides or sulfides from their unique states as before refined into reliable materials (Schweitzer, 2013). Moreover, Corrosion process is electrochemical in nature as the material exposed to the environment that contains water molecules which can leave electrons getting to be themselves positively charged particles and complete the electrical circuit (Roberge, 2006). These shows corrosion processes are time and temperature reliant as there is relations of materials with environment in terms of chemistry and electricity. Ion and concentration of corrosion cause the corrosion reaction or rates on materials (Schweitzer, 2013).

2.1.1 Corrosion Factors

According to Corrosion Inspection and Monitoring, 2006 there are four factors which could influence the corrosion. There are environment, temperature, stress and material factor (Roberge, 2006).

2.1.1.1 Environment Factor

The environment that concern to the corrosion is the area which contact with the metal surface. Local cells are a driving force that can cause corrosion problem as these local cells cause differences nearby on metal surface area. Then, the corrosion behavior cause by the presence of microbes as one of the environment factors as it influence the degradation of the materials. Figure 2.1 shows the effect of different microbes degradation mechanism on materials (Roberge, 2006).

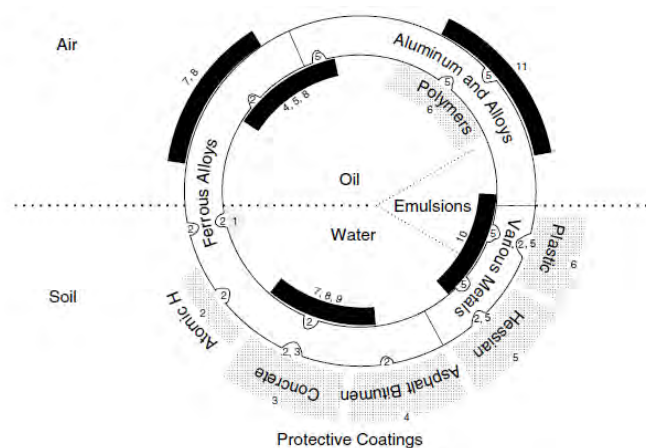


Figure 2. 1: The effect of different microbes and degradation mechanism (Roberge, 2006)

Moreover, flow effect is also one of the environment factors on corrosion. The demolition of protective film on the metallic surface caused by the flow effect due to the high flow rates. These also results more impact to the corrosion rate.

2.1.1.2 Temperature Factor

The tendency of corrosion is influenced by the temperature changing of the solution and the temperature is increases results the chemical reaction rate to be increases. The figure 2.2 below shows the effect of temperature and composition towards corrosion action of material that reveal to hydrochloric acid solutions.

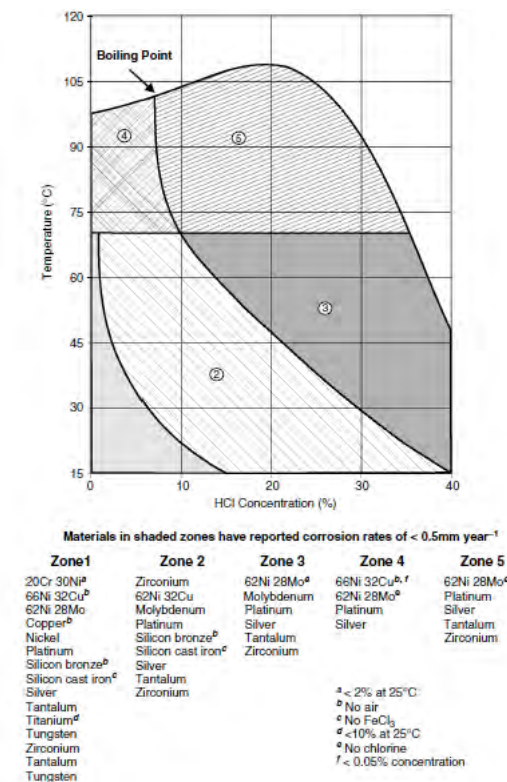


Figure 2. 2: Corrosion rate of metallic materials in HCl (Roberge, 2006)

2.1.1.3 Stress Factor

Stresses that result the environmental cracking caused by residual cold work, welding, grinding, thermal treatment, external service factor and must be tensile. The stresses caused by the collection of corrosion are typically formed in confine geometries where the particular volume of the corrosion product is larger than the metal that is corroded. Stresses from extending corrosion cause the proximate metals to flow in plastic manner (Roberge, 2006).

2.1.1.4 Material Factor

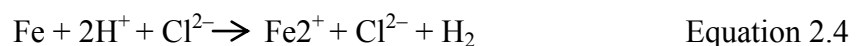
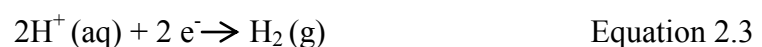
Unpredicted corrosion cause from the lack of material denotation. The composition of material grain boundaries is the material factor of corrosion. Most of the degradation reactions are through grain boundaries or started at grain boundaries. The presence and distribution of second phase result to the degradation reactions at grain boundaries or spread through the grains. Corrosion forms from the degree of the grain path. However, the grain structure is the factor that let the corrosion occur along grain boundaries. Long, wide, and very thin pancake-shaped grains are virtually essential for a high influence of the tendency to exfoliate (Roberge, 2006).

2.1.2 Corrosion mechanism

According to Fundamental of Corrosion, corrosion in aqueous solutions is common corrosion processes. Water, seawater, various process streams in industry provide in solution medium, moistures in the atmosphere and water in the soil effect to aqueous corrosion. So, water is rare in pure form while various salts and gases remain dissolved in it, and their separation makes the water as a conducting medium. This medium acts as an electrolyte and it comes in alkaline, acidic or neutral (Schweitzer, 2013).



The chemical reaction above shows corrosion reaction involves the oxidation of pure metal when it exposed to acidic solution. This pure iron reacts with hydrochloric acid and result chemical reaction and the electrolyte begin to bubble rapidly. The reactions result to iron to be gradually disappears and the hydrogen bubbles moving upwards to the electrolyte surface and there are exchanges of electrons taking place while on this chemical reactions.



The iron has been changed into the form of iron ion by release two electrons for oxidation reaction known as anodes while when the hydrogen ion was reduced by accepting the electrons, it known as cathodes and hydrogen gas is formed. The electrons transfer done on the metal surface. Anodes and cathodes with a complete electrical circuit will result a difference in electrical potential. The electrons flow in direction of from anode to cathode, as to complete the circuit the positively charged ions move toward the cathode. The current flow will be higher as the rate of corrosion is increases. Anodes and cathodes can be converted on the surface while the anodic areas moving uniformly over the metal's surface. Anodic reaction is when the metal is oxidized to a higher valence state and result in the formation of metallic ions. Anodic reaction is where the dissolution of metal occurred then the release electrons consumed in the cathodic process.

2.1.3 Corrosion Protection

According to ISO 8044:2015, corrosion protection is the modification of corrosion system. Corrosion system is the system which contains metals and the influence environment to corrosion. So, the corrosion protection would reduce the rate of corrosion damage. Moreover, according to Corrosion and Corrosion Protection book, corrosion protection is the methods, measure and procedure to evade the corrosion damage. Corrosion protection consists of active and passive. Figure 2.3 below shows the relation of active and passive corrosion protection.

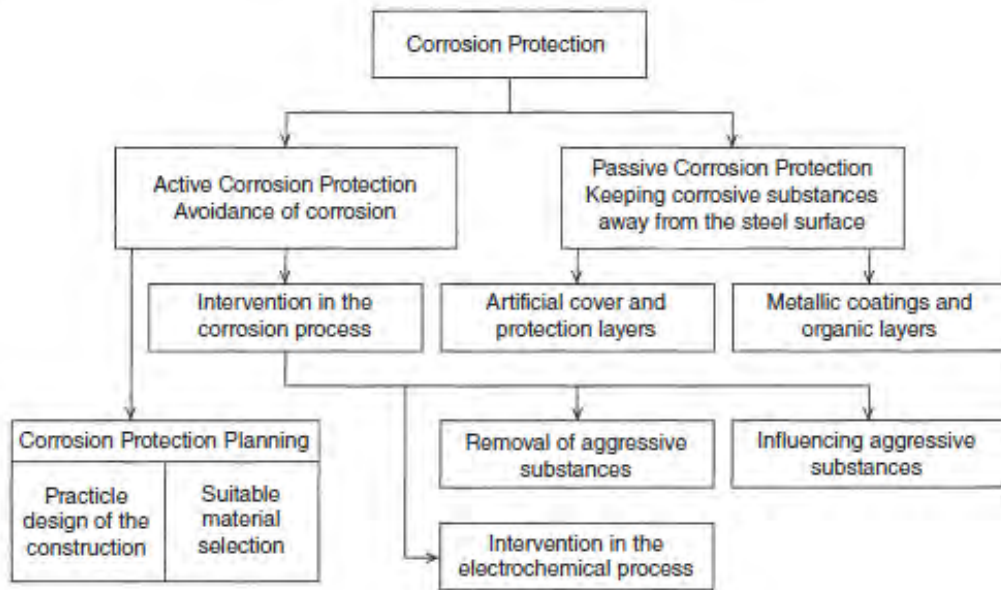


Figure 2. 3: Methods, measurement and procedure of corrosion protection (Maaß & Peißker, 2011)

2.1.3.1 Coating

ASM Metal Handbook Volume 13A: Methods of Corrosion Protection defines coating is the kind of surface protection between metal substrate and the environment from being oxidized. There are three type of coating which is organic, inorganic and metallic.

2.1.3.2 Galvanic Couples

Galvanic corrosion exhibit different metals immersed in the same electrolyte had electrical contact. The metal in the galvanic couple with the less corrosion potential has potential to be attracted to the positive direction by the metal that has the greater corrosion potential. This can result the metal with few potential can accelerate corrosion (P.Natashan, 2003).