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Corrosion Mechanism on Carbon Steel Coated with WC-10%Ni

Muhammad Mujibuddin Bin Mustain and Azzura Binti Ismail Faculty of Mechanical Engineering, University Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia

Abstract: Carbon steel is the most widely used engineering material and accounts for approximately 85% of the annual steel production worldwide. It is also used in many types of engineering application due to the excellent in mechanical properties and a better choice for the cost. However, the usage of carbon steel is limited to its corrosion resistance and tends to corrode easily when exposed to both oxygen and moisture. There is variety of protection that already been implemented to reduce the corrosion rate of the carbon steel including providing a coating with high corrosion resistance alloys. In this study, carbon steel was coated with WC-10%Ni and the corrosion mechanism was observed at different temperatures. The value of corrosion rate was observed from weight loss measurement and electrochemistry test by using potentiostat. The quantitative analysis by electrochemistry analysis using Tafel plot was explained the corrosion attack in terms of open circuit potential, corrosion potential, Ecorr and current density, icorr. The results reveal that temperature and time affect the corrosion rate on carbon steel coated with WC-10%Ni. The most severe attack was identified at the edge of base metal to WC-10%Ni coating interface. This is due to galvanic effect between dissimilar base metal and coating. The value of the Open Circuit Potential (OCP) also increased as the corrosion rate increased. The mechanism of corrosion attack and coating integrity by WC-10%Ni was observed by using an optical microscope and SEM.

Key words: Carbon steel, HVOF thermal spray, oxidation, cermet alloys, OCP

INTRODUCTION

The US Department of the global thermal spray coating market is expected to reach 12.29 USD billion by 2022. This anticipated growth result from the rising scope of end-use applications due to coating benefits that include wear and corrosion protection, low toxic gas emission, thickness capability and electrical resistance (Panossian et al., 2012). The growing need for corrosion resistant coatings in most top two application segments; aerospace and industrial gas turbines is expected to fuel demand over the next 7 year (Liu et al., 2012). In the oil and gas industry, it is common to transport the liquid or gaseous goods through undersea pipelines. Any penetration of the coatings can eventually result in leakage and environmental disaster. Therefore, for both corrosion prevention and protection, the pipes are typically coating up to 100 mm thick in total (Parker and Peattie, 1999). This study reveals the corrosion mechanism of carbon steel when coated with cermet alloys (WC-Ni). The most application of this coating technique is for oil and gas pipeline transporting hydrocarbon from off shore to on shore.

MATERIALS AND METHODS

The chemical composition of this carbon steel by wt.% consist of 0.035 C, 0.275 Si, 0.245 Cu, 0.100 Ni, 1.8 Mg, 0.01 P, 0.005 S and Fe (Liu *et al.*, 2012). The experimental comprises into two techniques; Tafel plot from the electrochemical method by using WPG100 potentiostat/galvanostat and weight loss measurement from immersion. The mechanical properties of the coating were identified by hardness test.

The size of the test sample for electrochemical corrosion testing was $12.7 \times 12.7 \times 10$ mm. A copper wire was inserted into the non-working surface and this surface was coated with epoxy. The artificial seawater was synthesized composed of 3.5% sodium chloride (NaCl) and the temperature starts with ambient room temperature (28 $\pm 1\,^{\circ}$ C). During the test, the scan rate was set at 1 mV sec⁻¹.

For weight loss measurement, the sample was immersed in artificial seawater for 5, 10, 15, 20, 25 and 30 day. After immersion complete, the samples were removed from the test solution and the corrosion products on the sample surface were removed with 500 mL deionized water and then dried. The samples were

measured with a Shimadzu microbalance. The average corrosion rate was equal to the ratio of weight loss (mg) to corrosion surface area (cm²) and time. The corrosion rate according to electrochemical analysis was determined from Faraday Law equation (Eq. 1 and 2).

The surface morphologies and chemical compositions were analyzed with (Nikon Eclipse) Optical Microscope and (JEOL JJSM-6380LA) Scanning Electron Microscope (SEM) respectively. SEM was also used to evaluate the microstructure, element composition and corrosion mechanism of the coating performance.

RESULTS AND DISCUSSION

Hardness test: The hardness test is conducted to determine the hardness of the coating on the sample. Three sample has been used to obtain the average hardness value. The hardness test was done by using Instron hardness tester. This hardness test was done at three different spots on top of the coating layer. The HRC value that was obtained is converted to HV value by using interpolation method. Table 1 shows the results of the hardness testing.

Immersion corrosion test: Immersion test was conducted in order to identify the corrosion rate of the exposed surface of the sample. Table 2 shows the immersion test results after 30 day of immersion.

The results from the immersion test above show the reduction of the sample weight for 30 day of immersion. The weight loss increased over the time where for the first 5 and 10 day the weight loss is not too obvious, however on 15 and 20 day there is significant different trend on the weight loss result of coated carbon steel due to the formation of corrosion product (rust) developed on metal surface was collapse and exposed the base metal to corrosion attack. After 25 and 30 day, the weight loss becomes greater again and more noticeable. The weight loss and the corrosion rate was calculated according to the Faraday's Law equation:

Table 1: Hardness value of the coating layer of WC-10%Ni

Table 1: Thirdness value of the county layer of 170 107 at 1			
No. of sample	Average (HRC)	Average (HV)	
1	7.63	186.52	
2	7.23	184.92	
3	8.87	191.48	

Table 2: Immersion test weight loss and corrosion rate results

Days	Weight loss (mg)	Corrosion rate (mm year ⁻¹)
5	0.00136	0.01304
10	0.01046	0.10026
15	0.01876	0.17981
20	0.01830	0.17540
25	0.02240	0.21470
30	0.02900	0.27796

$$CR = \frac{87.6W}{DAT} \left(\text{mm year}^{-1} \right) \tag{1}$$

Where:

W = Weight loss in milligrams (mg)

D = Density material (g cm $^{-3}$)

 $A = Area (cm^2)$

T = Time of exposure (h)

Figure 1 shows the graph of weight versus time of exposure for the immersion test. The weight loss is significantly increased when the time of exposure increase. It can be concluded that as the materials are exposed to corrosion media, the metal lost its weight in significant to time. But, after certain period, the corrosion product caused the weight increased compared to the weight before immersion was done. However, due to the porous structure of the product, it may collapse after certain period and it can be seen after 15-20 day. The collapse of the corrosion product may exposed the bare metal for further corrosion attack (after 25 day).

Electrochemical corrosion test: Figure 2 shows the combination of polarization curves for carbon steel at 28°, 40°, 60° and 80°C coated with WC-10%Ni in 3.5% artificial seawater. The Open Circuit Potential, OCP was increased as the artificial seawater temperature increased as expected. The OCP represents an initial value when metal is exposed to an electrolyte. This describes the finite amount of time to transform an air-formed oxide film on a metal surface into an Electrical Double Layer (EDL). Then the direction of potential change is determined by how EDL chemistry adjusts to accommodate electrolyte chemistry. This will elucidate how metal surface forms a passive film and protects the metal from further corrosion attack (metal self-healing, typically at increasing OCP).

Table 3 shows the results of Open Circuit Potential (OCP) and Corrosion Rate (CR) for the combined Tafel polarization curve at different temperature setup. The

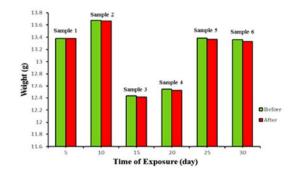


Fig. 1: Graph of weight vs. time of exposure

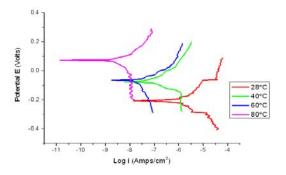


Fig. 2: Combined Tafel polarization curve of the carbon steel coated WC-10%Ni at different temperature

Table 3: Results of OCP and CR for the combined Tafel polarization curve at different temperature

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Temperature (°C)	OCP (V)	CR (mm year ⁻¹)
28	-0.210	0.074
40	-0.077	0.083
60	-0.065	0.089
80	0.072	0.101

data for OCP above was obtained from the Tafel plot meanwhile, the CR data was obtained by using Faraday Law:

$$CR = \frac{M}{nF\rho} xi_{corr}$$
 (2)

Where:

M = Material molecular weight for carbon steel (55.85 g mole⁻¹)

n = Number of equivalent exchange (2)

 $F = Faraday's constant (96500 (g.equiv)^{-1})$

 ρ = material density for carbon steel (7.87 g cm⁻³)

 $i_{corr} = \mu A \text{ cm}^{-2}$

The quantity β_a and β_c are referred to as the Tafel constant which is 120 mV. The weight loss on carbon steel coated with WC-10%Ni is significant to the corrosion rate that has been obtained from the Tafel plot.

For the electrochemical test, the data that has been obtained shows that the temperature increase will also increase the corrosion rate. This follows the Langmuir isotherm concept of a continuous monolayer of adsorbate molecules surrounded by a homogeneous solid surface. Figure 3 shows the relation between the corrosion rate with temperature changes which relates the Arrhenius relationship for carbon steel coated WC-10%Ni in 3.5% NaCl. The negative slop of Arrhenius plot indicates the activation energy was a positive value. Therefore, the metal atom must overcome the activation energy peak which indicates that only a part of metal with higher energy can be corroded.

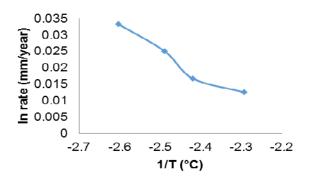


Fig. 3: Relation between the corrosion rate with temperature changes



Fig. 4: Surface condition of immersion test sample before test: a) coated and uncoated region and b) WC-10%Ni coating surface

Metallographic observation: For the metallographic observation, OM and SEM device was used in order to determine the condition of the exposed surface of the sample. For this research, the immersion test was observed by using OM meanwhile the electrochemical test was observed using SEM due to the condition after the electrochemical test is hard to be seen by using (OM). The corrosion mechanism for the electrochemical test is identified using the (SEM) device.

Figure 4 shows the both condition of the carbon steel coated with WC-10Ni at the exposed surface and at coating layer surface before the immersion test is conducted. The region between the coating layer and the region of the substrate metal can be seen clearly by using OM device. The color of the WC-10%Ni coating layer is changed from light grey to dark grey due to the oxidation during the sample cutting process using EDM wire-cut machine.

Figure 5 shows the condition of the sample surface after immersed into a 3.5%NaCl solution for 5, 10, 15, 20, 25 and 30 day. From the observation, for the first 5 day, the corrosion product occurs as the oxidation layer formed on top of the exposed surface of the sample. For the next 10 day the corrosion product still occurs but during the 15 and 20 day the corrosion rate was slow

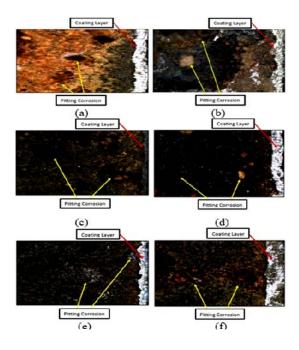


Fig. 5: Surface condition of immersion test sample after immersion test: a) 5 day, b) 10 day, c) 15 day, d) 20 day, e) 25 day and f) 30 day

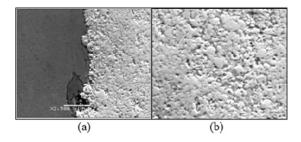


Fig. 6: Surface condition of electrochemical test sample before test: a) coated and uncoated region and b) WC-10%Ni coating surface

down and the corrosion product not formed on top of the metal surface. After 25 and 30 day, the corrosion product formed again on the metal surface and the weight loss increased.

The electrochemical test sample was observed by using SEM device in order to identify the corrosion mechanism that can't be seen by using the OM device. The corrosion reaction that formed on the electrochemical sample is not obvious as immersion test. Figure 6 shows the condition of the exposed surface of electrochemical test before and after the test.

Based on the observation, the WC-10%Ni coating layer coated by using HVOF thermal spray provide good coating surface and the level of porosity is minimum

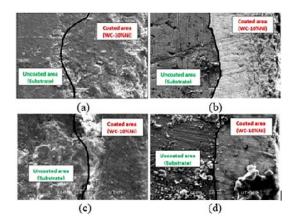


Fig. 7: Surface condition of electrochemical test sample after test: a) 28°C, b) 40°C, c) 60°C and d) 80°C

(Fauchais and Vardelle, 2012). This will provide a very good corrosion resistant to the substrate metal. Based on Fig. 7, the corrosion product formed on the exposed surface of the coated WC-10%Ni. At 28°, 40°, 60° and 80°C is not consistent. This is because there is gap between the sample with the resin mounting that let the 3.5%NaCl solution entering the gap during the electrochemical test and formed corrosion product. The corrosion reaction primarily on the uncoated area meanwhile the coated area only faced small corrosion reaction.

CONCLUSION

From the data that has been obtained from the weight loss measurement, it can be concluded that the general corrosion attack increased as the time immersion increased. This is because some exposed metal still attacked by corrosion even dome shape and surrounded area were covered by corrosion product. The corrosion products behave as protective layers only slow down the corrosion rate but not prevent further corrosion attack. The electrochemical analysis and optical observation reveals that increasing the temperature was increased the corrosion rate on carbon steel coated with WC-10%Ni. The corrosion attack mostly happens at the base metal and coating interface.

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