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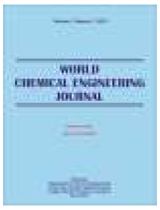

Temperature Effect on Corrosion Rate of Metal AA 5052 Using D-Galactose Inhibitors In Sulfuric Acid Media With Electrochemical Method

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ABSTRACT

Aluminum Alloy 5052 (AA 5052) is a metal that can be used as a biopolar plate in proton exchange membrane fuel cell (PEMFC), because it has the advantages of being resistant to corrosion, high conductivity, easy shape and light weight. PEMFC produces electrical energy and the rest of the process in the form of hot water and steam. In a bipolar plate PEMFC environment corrosion can easily occur due to an acidic environment and high operating temperature around 40°C-80°C. For this reason, a treatment is needed to strengthen the corrosion-resistant properties of AA 5052. The coating of the material can be done using the technique of electrophoretic deposition (EPD) using green inhibitor to reduce the corrosion rate. The electrochemical method was carried out to see how much influence temperature had on the corrosion rate of AA 5052. In this study, d-galactose green inhibitor with a concentration of 0.5 g, EPD time of 20 minutes was used, in a PEMFC environmental simulation in 0.5 M H2SO4 sulfuric acid medium, with test temperatures of 25°C (room temperature), 40°C, 60°C, and 80°C. From the results of the analysis using the electrochemical method, there was an effect of temperature on the corrosion rate of AA 5052 without an inhibitor layer of 0.3610 mmpy at room temperature and increased at 80°C 3.9527 mmpy. While AA 5052 which was coated with a d-galactose inhibitor, had a corrosion rate of 0.1678 mmpy at room temperature and continued to increase at a temperature of 80°C 3.7745 mmpy. Inhibitor efficiency was 53.51% at room temperature and decreased with increasing temperature to 4.5% at 80°C.

Keywords: *Aluminum AA5052 , Temperature, Electrochemical Methods, EPD, Corrosion*

1. INTRODUCTION

Currently, one of the technology development tools in the energy sector is the proton exchange membrane fuel cell (PEMFC). PEMFC is a fuel cell device that converts the chemical energy of hydrogen (H_2) and oxygen (O_2) into energy in the form of electricity, which has high efficiency and low emissions making it suitable for suppressing climate change [N. F. Asri *et al.*, 2017]. PEMFC has a humid and acidic environment inside, and has an operating temperature of 40°C to up to 80°C (313K – 353K) [F. Barbir, 2013]. Due to the high temperature and acidic environment of the PEMFC, it can cause corrosion of the bipolar plate [Pratiwi, W. D *et al.*, 2016].

One type of aluminum that can be used for the manufacture of bipolar plates is AA 5052, which has alloying elements of 2.2-2.8% Mg, 0.25% Si, 0.1% Cu, 0.1% Zn, 0.1% Mn, 0.15-0.35% Cr, 0.4% Fe. [T. Y. Chiang *et al.*, 2014]. AA 5052 has advantages such as high tensile resistance, easy to form, high conductivity and 65% lighter than steel [Pratiwi, W. D *et al.*, 2016]. The durability of PEMFCs can deteriorate due to mechanical degradation such as increasing the temperature of the membrane, resulting in a decrease in water content which results in corrosion of bipolar plates [T. Wilberforce *et al.*, 2019].

Temperature and humidity are the most important factors affecting the performance and durability of PEMFC [K. H. Hou *et al.*, 2012]. From this problem, it is necessary to control damage to PEMFC components, especially on bipolar plates which can corrode. Previous studies [Z. Luo *et al.*, 2006.] simulated the environment in PEMFC in the form of a 0.5 M H_2SO_4 solution.

Corrosion rate can be controlled by coating or cathodic protection using inhibitors and proper material selection [I. A. Arwati *et al.*, 2019]. Corrosion inhibitor is a corrosion inhibitor when added to a corrosive environment can inhibit the corrosion rate [F. Gapsari, 2017.].

The fast adsorption capacity physically and chemically on the metal surface confirms that the inhibitor is very good to use [Z. Havada *et al.*, 2017]. One way that can be used to protect metal AA 5052 using inhibitors to avoid corrosion is to use the electrophoretic deposition (EPD) technique.The principle of the electrophoretic deposition technique is to deposit charged particles that are dispersed in a suspension system due to the influence of an electric field [A. Peter *et al.*, 2017].

Inhibitors are divided into 2 types, namely organic inhibitors and inorganic inhibitors. In use as a corrosion rate control inorganic inhibitors are not recommended because they are toxic and can damage the environment. On the other hand, it is highly recommended to use organic inhibitors because they are made from natural and environmentally friendly ingredients. Gum arabic is one of the organic inhibitors because it is made from acacia sap, one of the natural saps collected from acacia trees that grow in sub-Saharan areas [B. Choudhary *et al.*, 2017]. Judging from the journal written d-galactose is a monomer of arabic gum. This means that d-galactose is also an organic inhibitor that is safe to use and environmentally friendly. In the PEMFC environment, temperature is one of the factors causing corrosion. In a previous study [K. Azzaoui *et al.*, 2017] using a d-galactose inhibitor coating on metal AA 5052 in a 0.5 M H_2SO_4 solution with a room temperature test temperature of 25°C, the results obtained a corrosion rate of 5,69527 mpy, the researchers will try to add temperature variations based on PEMFC operating temperature using the same test method and inhibitor concentration. On this basis, in this study, temperature variations will be studied to see the corrosion rate of AA 5052 metal which has been coated with d-galactose inhibitor in a simulated corrosive environment using a 0.5 M H_2SO_4 solution.

2. RESEARCH METHODOLOGY

The first stage of the research process was the preparation of the test metal and the preparation of the solution including the preparation of the test metal, the manufacture of a solution of d-galactose, the manufacture of pickling solutions of acids and bases, and the manufacture of a solution of 0.5 M H_2SO_4. The EPD process is a test metal coating process that has been prepared and has been cleaned using a pickling solution. The EPD process uses 0.5 g d-galactose inhibitor coating media. In the process using a voltage of 20 V, a current of 0.01 A, an immersion time of 20 minutes, is the best time for the EPD process [M. A. Abu-Dalo *et al.*, 2012].

Testing the corrosion rate using the electrochemical method using a potentiostat Electrochemical Workstation (model CS350). Corrosion rate testing was carried out on metals without inhibitor coating and inhibitor coated metals with temperature variations of 25°C, 40°C, 60°C and 80°C for each metal. Surface morphology testing using SEM tools and to see the layer thickness using a microscope, both were carried out at BATAN. The results of the EDS test will obtain the elemental composition on the metal surface.

2.1. Material and Material Preparation

Metal AA 5052 is cut to a size of 5 mm x 10 mm x 20 mm as shown in Figure 1, then the metal is drilled using a drill machine to be attached to a single copper cable as a conductor of electric current during the EPD process.

Fig. 1. AA 5052 which has been cut to a size of 5 mm x 10 mm x 20 mm

Sample sanding process with 600, 800, 1000, 1200 and 2000 grid sandpaper under wet conditions to smooth and clean the remaining dirt on the sample surface. Manufacture of metal cleaning fluids and cleaning methods using standards [ASTM, 1999]. For pickling acid mixture, namely HF 3.13 – 23.75 ml and nitrate 62.5 – 93.75 ml dissolved in 500 distilled water. The mixture for pickling base is NaOH 2.75 – 9.375 g and sodium phosphate 0.1 – 0.5 g which is dissolved in 500 ml of distilled water. Preparation of 0.5 g of d-galactose inhibitor solution dissolved in 1000 ml of distilled water. Simulation of corrosive environment using 0.5 M H_2SO_4 (98%) which means 27.19 ml of H_2SO_4 dissolved in 1000 ml of distilled water.

2.2. Electrodeposition Coating (EPD)

EPD is a material coating technique with the principle of deposition of charged particles that are dispersed in a suspension system due to the influence of an electric field. The electric current sourced from the DC power supply propagates from a positively charged metal (anode) to a negatively charged metal (cathode) as shown in Figure 2. In this study, the EPD process using a d-galactose inhibitor 0.5 g/l was carried out for 20 minutes with a voltage of 0.5 g/l. 20 V power supply, is the best time for the EPD process [M. A. Abu-Dalo *et al.*, 2012].

Fig. 2. EPD process using DC power supply

2.3. Corrosion Rate Analysis Using Electrochemical Method

Electrochemical testing using potentiodynamic polarization on metal AA 5052 was carried out to see the passive ability, characteristics of the d-galactose inhibitor and to determine the corrosion rate and inhibitor efficiency. This test uses the CorrTest Electrochemical Workstation (CS350) tool and uses three electrodes. Corrosion test solution using 0.5 M H_2SO_4 solution. Tests were carried out on metal AA 5052 without inhibitor coating and which has been coated with inhibitor, with test temperatures of 25°C, 40°C, 60°C and 80°C using a hotplate and thermometer as shown in Fig. Figure 3.

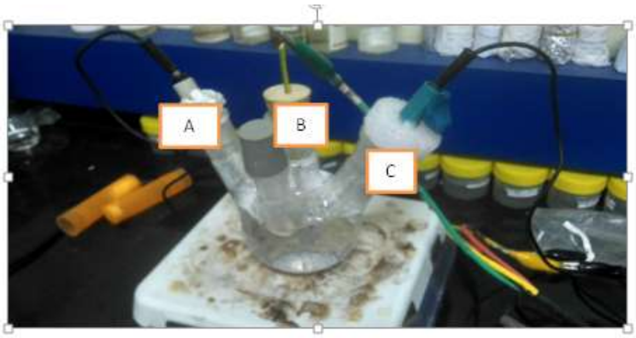

Fig. 3. The process of potentiodynamic polarization using temperature variations using a hotplate and thermometer, (a) auxiliary electrode (platinum), (b) working electrode (metal AA 5052), (c) reference electrode (AgCl)

In the potentiodynamic polarization test to determine the corrosion potential value (Ecorr) and the corrosion current density value (Icorr), using a potential range of -0.9 V to -0.1 V with a scan rate of 2 mV/s [M. A. Abu-Dalo,]. After the testing process, the results will be obtained in the form of data and graphs of potential (V) against current density (A/cm^2). Tafel analysis is used to determine the potential value of corrosion current (Ecorr) and the value of corrosion current density (Icorr). Before using Corr Test CS350, we must first know the density and specific weight of AA 5052, which can be seen in [ASM, 1999] to get the corrosion rate value. Calculation of the corrosion rate using the following equation:

CR = K1 x Icorr x EW/p
CR ; Corrosion Rate (mmpy)
K1 : 3.27 x 10-39MMPY G/ Acm^2
Icorr : (A/cm^2)
p : density (g/cm^3)
EW : equivalent weigght (g/mol)

2.4. Metal Surface Analysis

After electrochemical testing, samples without inhibitors and coated with inhibitors will be tested for morphology using SEM. The purpose of the EDS test was to determine the elemental composition on the metal surface of AA 5052 without inhibitor coating and coated with d-galactose inhibitor. The tool used is SEM-EDS Quanta 650 PSTBM BATAN which is shown in Figure 4 (a). EDS testing will produce data in the form of mass percentage, atomic percentage and so on. By knowing these various elements, it is possible to analyze the elemental composition on the metal surface of AA 5052 and the elemental composition of d-galactose which is the coating for AA 5052 metal.

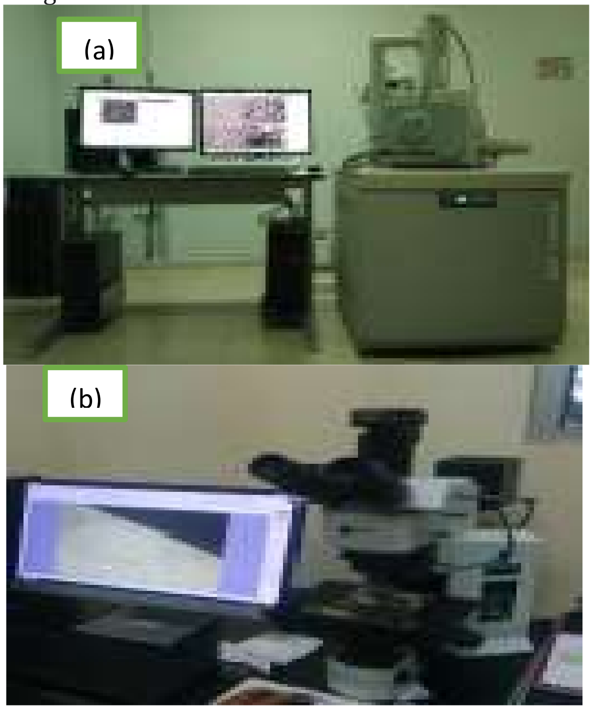

Fig. 4. (a) SEM-EDS Quanta 650 an (b) Olympus BX51 . microscope

After 20 minutes of EPD process using d-galactose inhibitor 0.5 g/l, the thickness of the AA 5052 sample was examined using an Olympus BX51 PSTBM BATAN microscope as shown in Figure 4 (b). At this stage, images are taken with a microscope connected to a computer using software to determine the state of the sample surface.

3. RESULTS AND DISCUSSION

3.1. Corrosion Rate Analysis Using Potentiodynamic Polarization Electrochemical Method

In this test, the potential range used for testing the corrosion rate using the electrochemical method with the potentiodynamic polarization technique is -0.9 V to -0.1 V, with a scan rate of 2 mV/s, at test temperatures of 25℃, 40℃, 60℃ and 80℃ at environment 0.5 M H_2SO_4. loss from the results of the calculation of the average value when the combined graph would show the difference in weight loss as in Figure 5 below:

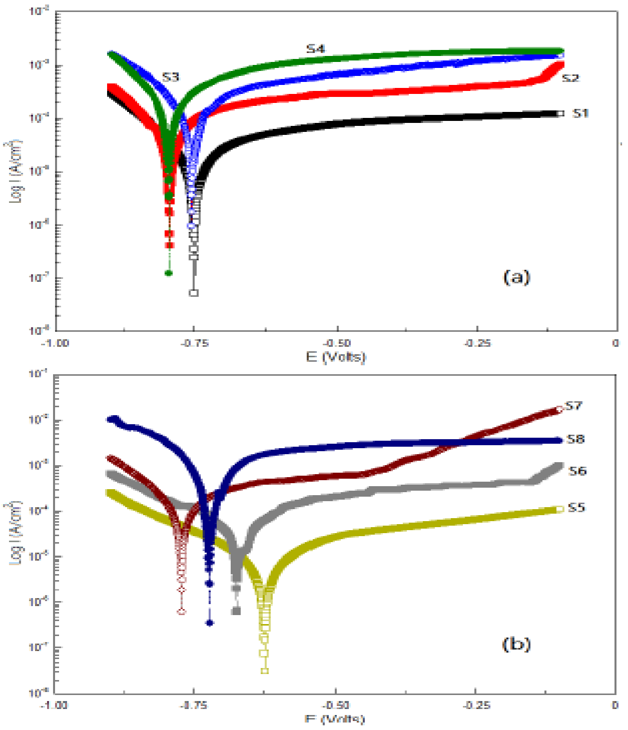

Fig. 5. Potentiodynamic log (I) vs. graph. potential (E) of metal AA5052 against an increase in ambient temperature of 0.5 M H_2SO_4. : (a) AA 5052 uncoated, (b) AA 5052 inhibitor coated.d-galactose

Figure 5 (a), (b) and Table 1 show that there is an increase in the corrosion rate with increasing temperature, but the corrosion rate value for the inhibitor-coated metal is lower than that of the non-inhibitory-coated metal. For metals without inhibitor coating, the original Icorr value was 3.2 x 10-5 A/cm2 sample (S1) to 3.5 x 10-4 A/cm2 sample (S4). In the inhibitor-coated AA 5052, the Icorr value decreased from 1.5 x 10-5 A/cm2 (S5) to 3.4 x 10-4 A/cm2 (S8). The decrease in Icorr value was caused by the adsorption of the d-galactose inhibitor molecule on the surface of AA 5052. The shift of the corrosion potential to a positive direction indicated that the d-galactose inhibitor was adsorbed in the anodic area thereby preventing the dissolution reaction of the metal. The ions in the d-galactose inhibitor layer will dissolve with sulfuric acid and damage the layer.

Table 1. Results of the potentiodynamic tafel a EPD using d-galactose inhibitor 0.5 g/l Analysis of AA 5052 before and after 20 minutes of

Sample	T (°C)	Icorr (A/cm2)	Ecorr (mV)	CR (mmpy)	Efficiency %
Uncoated	25	3.2×10^{-5}	-0.5529	0.361	
	40	1.7×10^{-4}	-0.5971	1.8905	
	60	3.1×10^{-4}	-0.5573	3.5184	
	80	3.5×10^{-4}	-0.5981	3.9527	
acosted	25	1.5×10^{-5}	-0.426	0.1678	53.51
	40	$1. \times 10^{-4}$	-0.4762	1.4638	22.57
	60	$2.\times 10^{-4}$	-0.574	3.2179	8.54
	80	2.9×10^{-4}	-0.5245	3.7745	4.5

The increase in temperature also affects the release of ions so that the layer damage will increase with increasing temperature. Due to the destruction of the inhibitor layer on the metal, it can accelerate the electric current flowing from the anode to the cathode and cause kinetic energy in the particles on the metal surface so that the d-galactose layer is eroded based on research and theory .

The efficiency of d-galactose inhibitor 0.5 g/l was 53.51% at room temperature and decreased with increasing temperature at 80°C to 4.5%. This indicates the presence of a physisorption inhibitor on the surface of AA 5052 which protects the metal from contact with the environment. When compared with research using Arabic gum inhibitor, the efficiency of the inhibitor obtained at room temperature was 81.3% and decreased with increasing temperature at 80°C to 23%. This shows that Arabic gum inhibitor is better.

3.2. Activation Energy Analysis

Activation energy analysis aims to determine the minimum energy for AA 5052 to corrode before and after EPD using d-galactose inhibitor 0.5 g/l for 20 minutes at a test temperature of 25°C - 80°C.

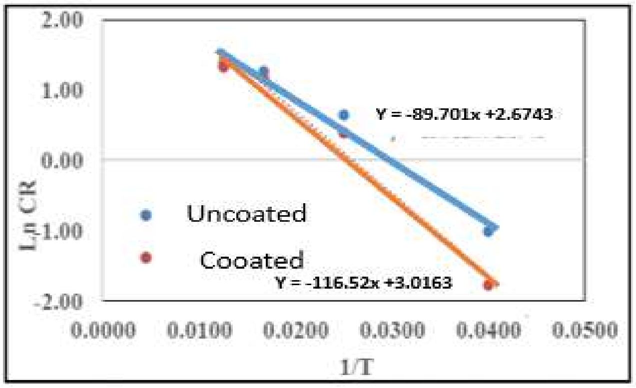

Fig. 6. Graph of LnCR vs. (1/T) AA 5052 before and after EPD with d-galactose inhibitors

Table 2. Comparison of LnCR vs. (1/T) AA 5052 before and after EPD with d-galactose inhibitors

Sample	T(°C)	1/T (x)	CR	LnCR (y)	x2	y2	XY
Uncoated	25	0.04	0.36	-1.02	0.0016	1.04	-0.04
	40	0.025	1.89	0.64	0.000625	0.41	0.02
	60	0.0167	3.51	1.26	0.0002778	1.58	0.02
	80	0.0125	0.16	1.37	0.0001563	1.89	0.02
Coated	25	0.04	0.16	-1.78	0.0016	3.19	-0.07
	40	0.025	1.46	0.38	0.000625	0.15	0.01
	60	0.0167	3.21	1.17	0.0002778	1.37	0.02
	80	0.0125	3.77	1.33	0.0001563	1.76	0.02

From the two line equations above, Figure 6 and Table 2, the activation energy value (Ea) of AA5052 before EPD was 745.8 J/mol, while the value of activation energy (Ea) of AA 5052 after EPD with d-galactose inhibitor was 968.6 J/mol. The activation energy (Ea) of AA5052 after the EPD inhibitor d-galactose was greater than the value of the activation energy (Ea) of AA5052 before EPD. The higher the value (Ea), the higher the energy required for corrosion to occur [I. A. Arwati et al., 2020]. The value of Ea for the corrosion rate on metal that has been coated with inhibitors is higher because the inhibitor forms a passive layer on the metal surface, so that the corrosion rate on the metal surface can be reduced due to the presence of a layer of resistance [P.O Ameh *et al.*, 2017]

3.3. SEM Morphology Results on AA 5052 to Increase in Temperature

At this stage, AA 5052 metal without testing, before and after coating was tested in a 0.5 M H_2SO_4 environment with a temperature of 80°C. The result is Figure 7 (a) AA 5052 without coating and before being tested on H2SO4 the metal grooves are visible in the direction and lighter, indicating that there is no adsorbed layer on the surface of AA 5052. Figure 7 (b) AA 5052 with an EPD inhibitor layer for 20 minutes was tested In the 0.5 M H_2SO_4 environment, a layer was seen on the metal surface, which indicated the presence of 0.5 g/l d-galactose inhibitor. If seen, the fine grooves on the protected metal indicate the presence of d-galactose inhibitor which is adsorbed on the surface and forms a passive layer, which this passive layer can reduce the corrosion rate.

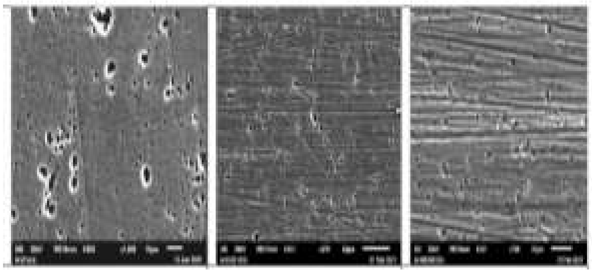

Fig 7. SEM results of AA 5052 (a) AA 5052 before testing, (b) inhibitor-coated AA 5052tested on H_2SO_4, (c) AA 5052 without coating tested on H_2SO_4

The increase in temperature affects the release of d-galactose inhibitor layer ions so that the surface of AA 5052 looks porous as shown in Figure 7 (b), it is a d-galactose layer which reacts with temperature increasing the formation of H_2 so that the layer is detached and not homogeneous. During the coating process on the cathode surface also formed H_2, therefore when the d-galactose layer was formed, H_2 was trapped in the d-galactose layer

While in Figure 7 (c) AA 5052 without coating tested on H_2SO_4 looks rougher, there is damage or corrosion in certain locales and inhomogeneous grooves, this happens because the increase in temperature can accelerate the anodic and cathodic reactions of metals [Sagir Ava *et al.*, 2020].

3.4. SEM-EDS results on AA 5052

In Figure 8 the SEM-EDS results show the presence of Mg elements of 4.94% while 95.06% of Al elements on the surface of AA 5052 before coated with d-galactose inhibitor and without being tested in H_2SO_4 environment, while in Figure 9 after the presence of inhibitor coating on AA 5052 metal it can be seen there are elements of O by 2.62%, Mg 4.68%, and Al 92.70%. The decrease in the percentage of Al content indicates the adsorption of polar O atoms on d-galactose which covers the surface of AA 5052 by physisorption [Abu Dalo et al., 2012].

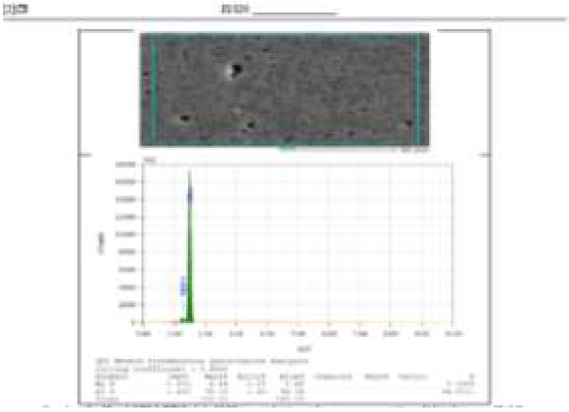

Fig. 8 . Results of SEM-EDS AA 5052 without coating and without testing in H2SO4 environment

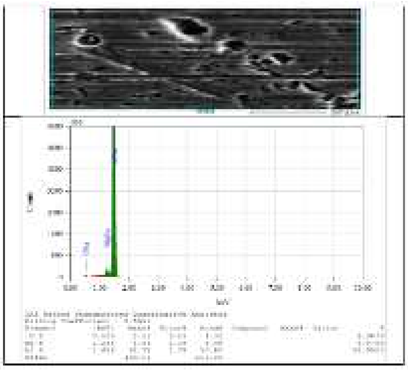

Fig. 9. Results of SEM-EDS AA 5052 inhibitor coated and tested in H_2SO_4 environment

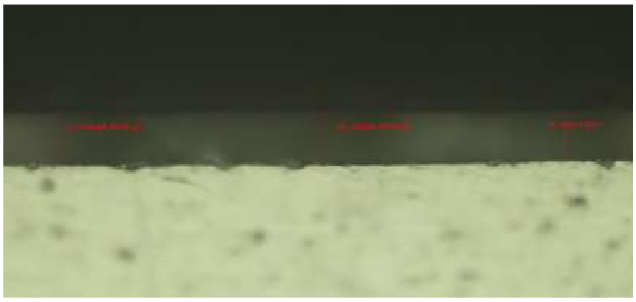

Fig 10. Morphological results of d-galactose inhibitor layer thickness on AA 5052

Figure 10 shows that the 20-minute EPD layer produces layers with varying thicknesses ranging from 22.78 m – 23.55 m. This layer protects the metal from direct contact with the environment. This is in accordance with the theory [I. A. Arwati *et al.*, 2020], research, that the EPD process will produce a layer thickness ranging from 0.1 - 100 m. The layer is adsorbed by physisorption [B. Choudhary *et al.*, 2018].

4. CONCLUSION

With the effect of temperature, the corrosion rate of AA 5052 without coating is 0.3610 mmpy at room temperature and increases at 80°C by 3.9527 mmpy, while AA 5052 which is coated with d-galactose inhibitor has a corrosion rate of 0.1678 mmpy at room temperature and continues to increase at room temperature. 80°C at 3.7745 mmpy. The inhibitor efficiency was 53.51% at room temperature and decreased with increasing temperature to 4.5% at 80°C.

The results of the surface morphology using SEM on inhibitor-coated AA 5052 showed a porous surface, it was the d-galactose layer which reacted with temperature increasing the formation of H_2 so that the layer was detached and not homogeneous. While AA 5052 before EPD showed damage or corrosion in certain locales and inhomogeneous grooves. The results of the SEM-EDS AA 5052 test without a layer of Al elemental mass of 95.06% and Mg of 4.94%, while after coating with EPD using a d-galactose inhibitor, 2.62% of O elements were adsorbed on the surface of AA 5052 and reduce the element Mg 4.68% and Al 92.70%.

Observation of the thickness of the d-galactose layer on AA 5052 using the EPD coating technique for 20 minutes resulted in layers with varying thicknesses ranging from 22.78 m – 23.55 m. The coating is adsorbed by physisorption, thus protecting the metal surface in direct contact with the environment.

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