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Corrosion rates and pore sizes on anodized aluminum 6083 with different voltages using citric acid anodizing process

Burhanudin Candra Wicaksono[a], Moch. Syamsul Ma'arif[b*], Iis Siti Aisyah[c], Wahyu Caesarendra[d]
[a,b] Department of Mechanical Engineering, Universitas Brawijaya
Malang, Indonesia

[c] Department of Mechanical Engineering, Muhammadiyah University of Malang
Malang, Indonesia

[d] Faculty of Integrated Technologies, Universiti Brunei Darussalam
Brunei Darussalam

Email of the corresponding author: syamsulm@ub.ac.id

Abstract

Aluminum alloy such as Al6083 series has a good properties in forming, welding, machining and corrosion resistance. During life cycle of engineering products such as ships, pipes or others which operate on-shore or off-shore, sea water become cause factor of metal corrosion because it induces corrosive environment to metal. In this case then the product need a necessary techniques to prevent corrosion, one of them is by coated it through anodizing processes. In this research, pore sizes and corrosion rate of anodized aluminum 6083 alloy was studied by varying the operating voltage of process of 15V, 20V, and 25V. The other variables were controlled during the research, i.e. electrolyte temperature within ranges of 28 ± 2ºC, electric current of 1 A, distance between the anode and cathode of 20 mm, processing time for 10 minutes and using 15% of citric acid ($C_6H_8O_7$) as the electrolyte solution. The pore sizes were acquired by taking photos and automatic data display feature to determine pore sizes using the FlexSEM 1000 II apparatus. Data on corrosion rate data were collected using the Autolab PGSTAT204 apparatus. From the results it is known that using citric acid as an electrolyte during the anodizing process obtained an optimal point at a voltage of 20V with the largest pore size of 65.8 nm and a corrosion rate value of 0.00533 mm/year. This shows that increasing the voltage to certain value and using citric acid ($C_6H_80_7$) as an electrolyte can improve corrosion resistance due to the formation of aluminum oxide on the surface of the specimen.

Keywords: anodizing, citric acid, voltage, aluminum oxide, size of pore, corrosion rate

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1. Introduction

Human need for metal is ever increasing, because metal can be applied in various fields. One of the most widely used metals is aluminum. The aluminum 6083 series alloys are used for various application such as architectural applications, bicycle frames, vehicle or vessel for transportations, and welding structures [1]. When using aluminum for transportation vehicle, it will come into direct contact with the environment. One of the main causes of damage to transportation vehicle, e.g. ship hulls, is sea water itself because it induce corrosive environment to metal. In this case, therefore prevention of corrosion is needed. One of the means to prevent corrosion is by applying anodizing coat into metal.

All industries that use the strength-to-weight ratio see the anodizing process as an important means of finishing various manufactured products, with a strong and beautiful anodic oxide to provide corrosion protection, wear resistance and in many applications, a decorative appearance [2] [3].

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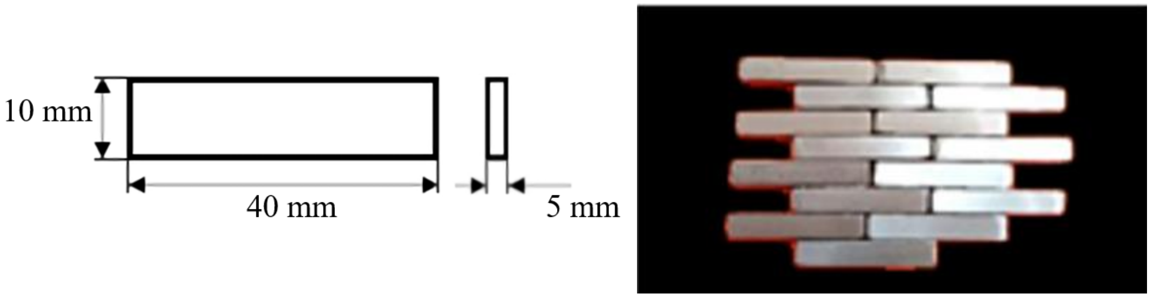
In previous research on the variation of concentration of citric acid [4], variations of voltage [5] on anodizing of aluminum was shown that aluminum with a purity of 99% such as Al 6083 was used as specimens. In others research works, anodizing process using sulphuric and citric acid solution with a concentration of 15%, combined with voltage of 15V, 20V, and 25V were conducted with a good results [6][7]. Those researches demonstrate that anodizing can be conducted on laboratory scale of simple anodizing baths. To show the pores sizes then Scanning Electron Microscope (SEM) was employed on the sample to obtain data on the width of the pores formed during the anodizing process. Anodizing process with voltage of 15V gave result of an average pore width of 8.05 µm. The process with voltage of 20V gave results of an average increase in the pore width value of 12.45 µm. When increasing the voltage to 25 V results in an increase in the average pore width formed of 19.52 µm [5].

The research above uses different variations of voltage in the anodizing process, while the electrolyte solution used for the anodizing process is sulphuric acid. Therefore the research was investigate the use of citric acid as electrolyte solution ($C_6H_8O_7$) on the pore size of the oxide layer and the corrosion rate of anodizing products. Therefore, this research will address the effect of the anodizing voltage on aluminum 6083 with citric acid electrolyte ($C_6H_8O_7$) on the corrosion rate and pore size.

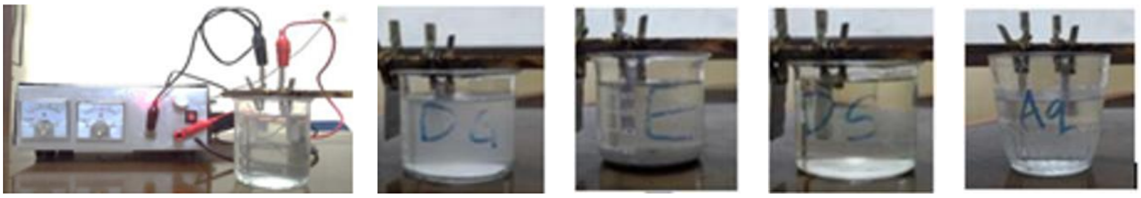
2. Methods

In this research, the experimental method was employed. The 6083 series aluminum used as an anode has dimensions of 40 mm × 10 mm × 5 mm. The independent variable used for anodizing is by varying the voltage at 15V, 20V, and 25V. Meanwhile the controlled variables were the temperature of the electrolyte of 28 ± 2ºC, electric current of 1 A, distance between the anode and cathode of 20 mm, anodizing process time of 10 minutes and concentration of the sulphuric acid as electrolyte solution of 15%. Dependent variables of this research are corrosion rate and pore size on the surface of the oxide layer.



(a) (b)

Figure 1.Aluminum 6083 specimens (a) dimensions, (b) photo of specimens



(a) (b) (c) (d)

Figure 2. Anodizing process apparatus: (a) anodizing bath, (b) degreasing (DG), (c) etching (E), desmutting (DS), (d) flushing with aquades (AQ)

Before carrying out anodizing processes, the aluminum surface is smoothed using sand paper with sizes 500, 800, 1200, 1500, 2000, after which pre-treatment is carried out. The pre-treatment consists of degreasing, etching and de-smutting which is intended to remove dirt on the surface of the specimen, in which anodizing is carried out later [8] (Figure 2.b).

After the specimen is ready then continues with the anodizing process in an electrolyte solution containing citric acid with a concentration of 15% (Figure 2.a). The anodizing process is carried out for 10 minutes. After the anodizing process, the specimen is washed. The first test is a corrosion rate test using an Autolab PGSTAT204 potentiostat apparatus connected to a computer and NOVA 1.11 software (Figure 3.a). For this purpose, specimens are dip into NaCl solution. To obtain the size of the pores, the second test of SEM test was carried out (Figure 3.b).

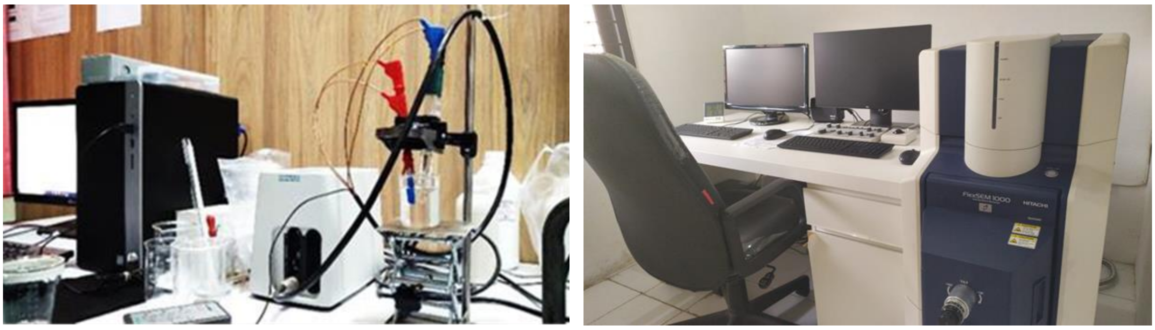

(a) (b)

Figure 3. Apparatus for the research (a) Autolab PGSTAT204 potentiostat*, (b) FlexSEM 1000 II Scanning Electron Microscope (SEM)*

3. Result and Discussion

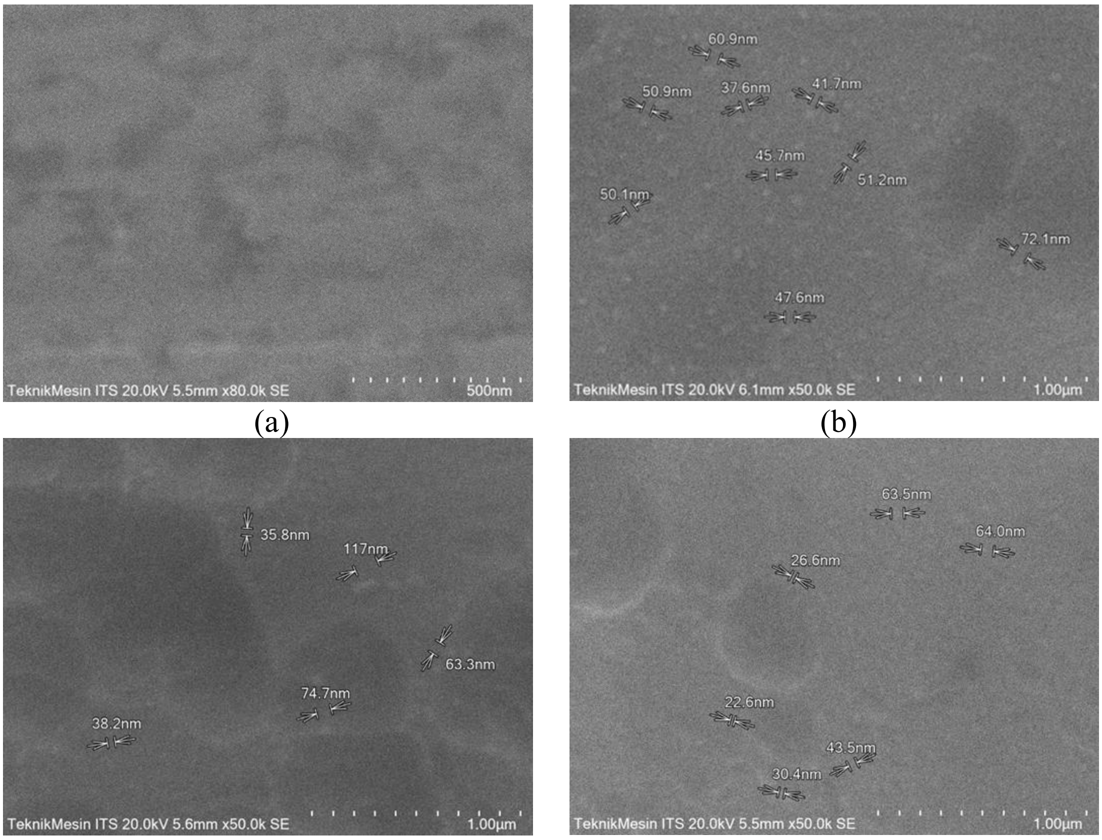
Size of pores

SEM photos were taken using the FlexSEM 1000 II. The SEM photos have aim to support the corrosion rate testing data. Pore size data from SEM photos can be seen in Table 1.

Table 1. The sizes of pore based as given by SEM

Voltage	Size of pores (nm)					Average (nm)
	I	II	III	IV	V	
No treatment	-	-	-	-	-	-
15V	60.9	50.9	50.1	37.6	41.7	48.24
20V	35.8	38.2	74.7	117.0	63.3	65.80
25V	63.5	26.6	22.6	43.5	30.4	37.32

From the test results, as shown in Table 1, for a voltage of 15V, the average pore size is 48.24 nm. In this voltage variation, small pore sizes because still in pore initiation stage was occurring. The pore size on the surface increases along with the increasing of voltage. The optimal pore size (biggest ones) was obtained at a voltage of 20V marked with increased pore size of 65.8 nm. The greater the voltage given, the faster and more abundant the formation of aluminum oxide on the anode surface will be. This is caused by the faster speed and intensity of transfer of electron/ion charge from the cathode to the anode. Meanwhile, on the voltage variation of 25V, there was a decreased of pore size of 37.32 nm.



(a) (b)

(c) (d)

Figure 4. SEM-micrograph of anodized Al 6083 (a) un-anodized, (b) with voltage of 15V, (c) with voltage of 20 V, and (d) with voltage of 25 V

Figure 1 is a photo of a specimen using Scanning Electron Microscopy (SEM) with a magnification of 50,000 times. Figure 1 (a) is a photo of a specimen without treatment. It can be seen that on the surface of the specimen there are still no visible pores even at a magnification of 50,000 times. Figure 1 (b) shows the results of anodizing with a voltage of 15V. It can be seen that the pores on the surface are small because still in pore initiation stages. In this variation, pore sizes ranged from 37.6 nm to 60.9 nm with an average pore size of 48.24 nm. Meanwhile, the result of photos of specimens with variations of voltage of 20V is shown in Figure 1 (c). In Figure 1 (c) it can be seen an increase in pore size from 35.8 nm to 117 nm with an average pore size of 65.8 nm. Figure 1 (d) is the photo of a specimen with variations in the voltage of 25V resulting in pore sizes ranging from 22.6 nm to 63.5 nm with an average pore size of 37.32 nm. From the data in Table 1 and Figure 1, it can be seen that the largest pore size is found in the specimen with a voltage variation of 20V with an average pore size of 65.8 nm compared to other variations. It can be seen that the increase in the width of the pores formed is directly proportional to the increase in the applied voltage [5].

An increase in the amount of aluminum oxide in anodizing process occurs due to an increase in the process voltage. The higher the voltage, the faster and more abundant the formation of aluminum oxide on the anode surface will be [9]. Higher voltage will make charge transfer speed faster and in greater intensity from the cathode to the anode. This will trigger the faster movement of negative oxide ions and hydroxide ions towards the anode. On the other hand, at the anode, with a large voltage, the oxidation rate at the anode will be faster so that the formation of Al^{3+} ions will be faster.

However, it can be seen that there is a significant decrease in the value of the pore size in the 25V voltage variation, this variation also has a smaller pore size compared to the other voltage variations, i.e. 15V and 20V. This is because the use of citric acid ($C_6H_8O_7$) as an anodizing solution has an optimal point in which in this research appears to be at a voltage variation of 20V. So if a voltage of more than 20V is applied, it can reduce the results of anodizing.

This is due to charge migration events occurring during the anodizing process. Hydrogen ions from citric acid move towards the cathode and undergo reduction reaction to form hydrogen gas. Negative ions in the solution such as citric acid ions move towards the anode. At the aluminum metal anode, an oxidation event occurs which causes the aluminum metal to oxidize to Al^{3+} ions. When Al^{3+} ions begin to form on the anode surface, these ions react with citrate ions which move towards the anode to form a layer of aluminum oxide.

At the beginning of the oxide layer formation process (stage 1), there is a decrease in current which indicates the formation of a barrier layer [10]. This decrease in current occurs due to forming of aluminum oxide on the aluminum surface, resulting in a thickening of the layer and causing the resistance to become greater. After the barrier layer thickens, seeds begin to form (stage 2). These seeds formed because the oxide layer which is an insulator is subjected to high voltage. When the oxide layer is damaged, it will create pore seeds near the boundary between the oxide and the solution. At this stage there is a decrease in current in the system and it will reach a minimum point when this stage stops. The next stage, i.e. initiation pore (stage 3), be marked as the beginning of the formation of the porous oxide layer structure. The pores formed at this stage are not perfect and there is an increase in current flowing through the system along with the refinement of the oxide layer structure. The increase in current occurs until the flowing current will be constant. It occurs when the oxide layer structure has been completely formed (stage 4). In this final stages (stage 4), the wide pores formed in this anodizing layer and can prevent further corrosion reactions. Therefore, this layer can protect the metal underneath by acting as a barrier from corrosive environmental attacks.

An explanation of why the size of pores is widest when applying a voltage of 20V is the dependence of the pore formation to the electric field produced by the increase in voltage during the anodizing process. Applying a voltage that exceeds a voltage of 20V will cause decay of the oxide layer on the surface of the specimen. Decay due to an electric field concentrated in the barrier layer causes an increase in temperature, thereby triggering the decay process of the oxide layer. The dissolved oxide layer is also getting bigger, so that the oxide layer that forms will decay back into the electrolyte solution will also be bigger [11].

Corrosion test

The second test on product of anodizing process is corrosion test. The test is an important one because it will reveal the influence of variation of voltage to corrosion behaviour of the aluminum oxide. A simulated environment in NaCl solution was chosen to imitate corrosion environment. Corrosion rate data was collected using the Autolab PGSTAT 204N apparatus. Corrosion rate results data can be seen in Table 2.

Tabel 2 Result of rate of corrosion test

Voltage (V)	**βa (V/dec)**	**βc (V/dec)**	**Ecorr, Calc (V)**	**jcorr (A/cm^2)**	**Icorr (A)**	**Corrosion rate (mm/year)**
No treatment	0.017398	0.013551	-1.0834	$1,33.10^{-7}$	$1,33.10^{-7}$	0.0148072
15V	0.012858	0.040831	-0.9667	$7,15.10^{-7}$	$7,15.10^{-7}$	0.0079726
20V	0.030351	0.038945	-1.1569	$4,78.10^{-7}$	$4,78.10^{-7}$	0.0053296
25V	0.085179	0.144582	-1.2895	$8,82.10^{-7}$	$8,81.10^{-7}$	0.0098278

It can be seen that the specimen with a voltage of 15V has a corrosion rate of 0.007878 mm/year, then for the specimen with a voltage of 20V it has a corrosion rate of 0.00533 mm/year, and finally for the specimen with a voltage of 25V it has a corrosion rate of 0.009828 mm/year. It can be seen that the increase in the width of the pores formed is directly proportional to the increase in voltage of the process. It also shown that the voltage of 20V has the best value of corrosion rate compared to other variations of 0.00533 mm/year. A decrease in the corrosion rate until voltage of 20V caused by an increase in the produced oxide layer. This happens because the greater the electric voltage used, the wider and more perfect pores in oxide layer. When the voltage becomes higher, the movement of electric charges will increase [12]. The increased movement of electrical charges will make it easier for ions to move on the surface of aluminum 6083 as a result of anodizing so that a stable and continuous oxide layer is formed on the entire Al metal surface. Increasing of the size (width) of the anodizing pore can prevent further corrosion reactions from occurring. However, when voltage is increased higher than 20V it can be seen that there is a significant increase in the corrosion rate value of 25V variation. On this variation, the corrosion rate value is only lower than un-treated aluminum 6083. This shows that the use of citric acid ($C_6H_80_7$) as an anodizing solution has an optimal point at a voltage of 20V. Based on the research, if a voltage of more than 20V is applied then it can reduce the corrosion rate of anodizing product.

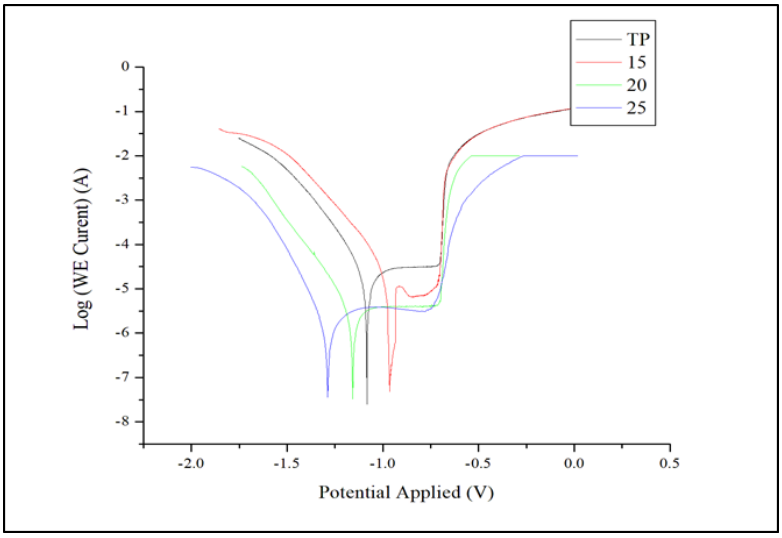


Figure 5. Tafel polarization curve of corroded Al 6083 in 3.5% NaCl solution

TP = un-anodized, 15 = 15V, 20 = 20 V, and 25 = 25 V

In the area of potential curve of cathodic reaction, reactions occur in the form of reduction of oxygen and reduction of alloy-forming metal ions. In the area of potential curve of the anodic reaction, starting from the corrosion potential (E_{corr}), a quite reactive oxidation reaction occurs, characterized by a sloping polarization curve or an increasing shift in current density [13]. From Figure 5, it can be explained that the further to the right, the physically it becomes more anodic and vice versa. Meanwhile, the lower the curve, the lower the corrosion rate value will be. Because the lower the position of the tafel, the smaller the I_{corr} value will be and the corrosion rate also decreasing [14] [15]. Corrosion rate testing using the electrochemical method with polarization of the free corrosion potential can be calculated using a formula based on Faraday's Law as below [14]:

$$CR = K\,\frac{a.i}{n.D}\ mmpy \tag{1}$$

Where:
CR = Corrosion rate
K = Constant (0.00327 mmpy)
a = Atomic weight of corroded metal (gram/mol)
i = Current density ($\mu A/cm^2$)
n = Number of electron releases on corroded metal
D = Density of corroded metal ($gram/cm^3$)

From Figure 5, it can be seen that the voltage variation of 20V has the steepest slope. This means that the activation energy required for corrosion to occur is very large so that the reaction rate becomes slower. The next steepness was experienced by a voltage variation of 15V, then a voltage variation of 25V and finally the specimen without treatment. The wear rate of each specimen also follows this slope sequence. When we pay attention to value of E_{corr} and the difference between the values of the corrosion potential (E_{corr}) and $E_{breakdown}$, the sequence becomes 25V voltage variation, 20V voltage variation, no-treatment variation, and finally 20V voltage variation. This data shows that all variations is susceptible to corrosion in the electrolyte tested.

4. Conclusion

Based on the results of research that has been carried out on the effect of different voltage for anodizing process of Aluminum 6083 with citric acid electrolyte ($C_6H_8O_7$), it can be concluded that the largest pore size is found in the specimen with a voltage variation of 20V with an average pore size of 65.8 nm. As the voltage increases, the corrosion rate of anodized Aluminum 6083 becomes lower, which indicates that the corrosion resistance of aluminum is getting better. However, it can be seen that the specimen with a voltage variation of 20V has the best value compared to other variations with a corrosion rate of 0.00533 mm/year. Therefore, the most optimal voltage variation for anodizing processes of Aluminum 6083 with use of citric acid electrolyte ($C_6H_8O_7$) is obtained at a voltage of 20V.

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