CORROSION CHARACTERIZATION OF ANODIZED AA 6061

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In this study we examined the effect of topography and corrosion resistance of aluminum alloy 6061 which has been anodized on a mixture of phosphoric acid and oxalic acid by using titanium cathode. Surface topography was tested with the N8 NEOS Bruker, corrosion testing performed by Tafel method using a potentiostat Autolab (PGSTAT302N), while testing the immersed test to determine the condition of the surface corroded done using 3.5% NaCl fluids with immersion time of 500 hours. The results obtained indicate that the change in the surface is affected by the potential applied during anodization process. Increasing the potential shown to improve the contour of the growing prevalence of pore sizes formed after the anodizing process. The corrosion resistance is also increased with increasing potential.

KEYWORDS

surface topography, potential, corrosion resistance, anodizing, AA 6061

1 INTRODUCTION

The general definition of biomaterials is a substitute material used to replace parts of living systems or to function in ties with living tissue [Yousefpoura 2014]. This material can be derived from natural or synthetic materials that are used over a certain time span on part or all of the system to replace tissues, organs or body functions [Ratner 1996]. However, biomaterials have deficiencies when compared to organs, such as the absence of complex responses such as organs in general. Biomaterials have only a single response. In addition, there is also a tissue response after the installation of biomaterials in response to toxins and foreign responses to the body. Some materials that can serve as biomaterials include polyethylene, titanium mesh, hydroxiapatite, high density polyethylene and polymethyl methacrylate [Purnomo 2016].

One type of material made of metal and often used for implant to replacing parts of the body that are permanently damaged or not is titanium [Ghazvinizadeh 2011]. This kind of material has osseointegration ability, that is the ability to attach to the surrounding tissue [Massaro 2002]. In addition, this material is also able to interact with living cells or tissue without causing a toxin reaction or trigger an immune reaction when used and able to withstand a very good mechanical load.

On the other hand, aluminum is one of the non ferrous metals with the widest application and available in various forms ie casting, wrought, rolling and extrusion [Wheeler 2012, Afrasiabi 2014]. In addition to being widely applied to a variety of manufacturing and automotive industries, this material also began to be applied to the medical world that anodic aluminum oxide (AAO) membrane is very well used for drug delivery and biomaterial applications [Ali 2013]. In addition, AAO membranes have also been used for cell interface substrates for biomaterial applications [Bruggeman 2013].

One way that can be used to create an anodic layer in a material is to perform anodizing process. This process has been used in the industry to protect metal components from corrosion since 90 years ago [Poinern 2011]. During the electrochemical process takes place, the levels of the chemical elements on the surface will be changed through the process of oxidation to produce an oxide layer thick enough to withstand further oxidation [Bensalah 2011, Setyarini 2017]. Two kinds of anodic aluminum oxide layers formed during the anodizing process. The first is a non-porous, thin and hard called barrier layer. Second, the structure of porous thicker oxide is commonly called anodic oxide layer.

The use of different materials to the parent metal with the aim of strengthening the oxide layer which will increase the corrosion resistance has not been widely discussed. Some examples of the use of different metals in anodizing aluminum processes are by using platinum [Araoyinbo 2010] and lead [Raj 2014] as cathodes. Meanwhile, there is research that uses Mg as the anode and a stainless steel as the cathode [Tu 2012].

One of the metals that can also be used as a cathode in the anodizing process is titanium. Titanium is known as a metal with its wide application because it has good mechanical properties, excellent corrosion resistance and biocompatibilty [Veys-Renaux 2016]. A research on anodizing aluminum using titanium as a cathode was performed by Setyarini, et.al. who reviewed the surface morphology and impedance properties of aluminium after being anodized [Setyarini 2016]. Based on this, the development of the anodizing process using other materials, especially titanium, as a cathode can be further developed and needs to be studied in more depth about surface topography and how much increase in corrosion resistance after being anodized.

2 MATERIALS AND METHOD

The experiment was perfomed with AA 6061 with the following composition (wt %): Mg 1.01%, Si 0.88%, Fe 0.2%, Cu 0.21 %, Zn 0.08%, Ti 0.08%, Mn 1.01%, Cr 0.05%, Al balance. Titanium was used as the counter cathode with a composition (% Wt) 2.6% P, 2.43% Ca, 0.54% Fe, 92.2% Ti, 0.29% Ni, 0.14% Zn, 0.90% Tm.

The aluminum alloy is connected to the anode and immersed in an electrolyte solution which is a mixture of phosphoric acid and oxalic acid. Solution temperature was kept constant in the range of 0-5^{0}C to the distance between the cathode and anode 5 cm and anodizing process time of 60 minutes.

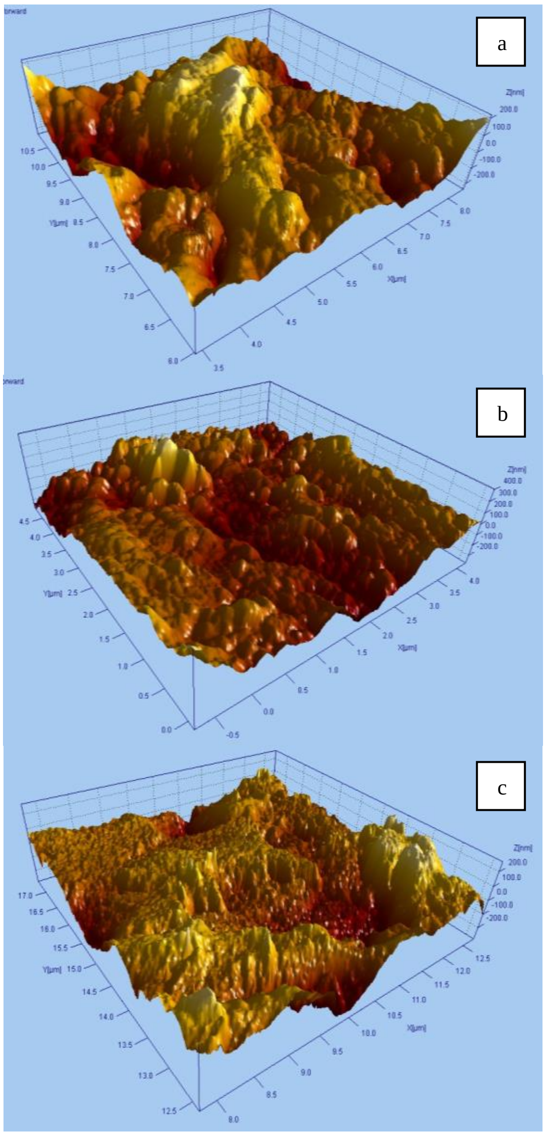
To determine the surface topography used by the N8 NEOS Bruker piezoelectric tube scanner that will control the direction of motion of x, y and z at the time of the scan process with the sensor needle tip will move back and forth along the surface of the specimen. The deflection of the needle will be detected by using a laser that bounced off the tip and towards the photo diode laser through a mirror. Furthermore, the photo diode and piezoscanner connected through via the feedback loop, then the mapping will appear on the computer.

During the process of electrochemical tests, three cells of electrodes were used, with the result of anodizing film layer as the working electrode, saturated calomel electrode as the reference electrode and platinum as the counter electrode. Volume ratio of 3.5% NaCl with a degree of acidity 7.03 with exposed sample area of $1 cm^2$. Potentiodynamic polarization test using a potentiostat Autolab (PGSTAT302N) at the temperature of 25 ± 10ºC. The scanning process was carried out at a rate of 1 mV / s.

Testing of corrosion rate with the method of immersed test was conducted after the entire sample underwent the anodizing process, it was cleaned with distilled water and dried. Furthermore, each sample was placed separately in the containers of 500 ml of 5% Sodium chloride solution for a period of 500 hours (21 days).

3 RESULTS AND DISCUSSION

Fig. 1 (a) shows surface topography on anodized aluminum substrate. Fig. 1 (b), (c), (d), (e) shows the aluminum substrate tested by using a potential difference. Fig. 1 (b), (c), (d), (e) shows the aluminum substrate tested by using a potential difference.



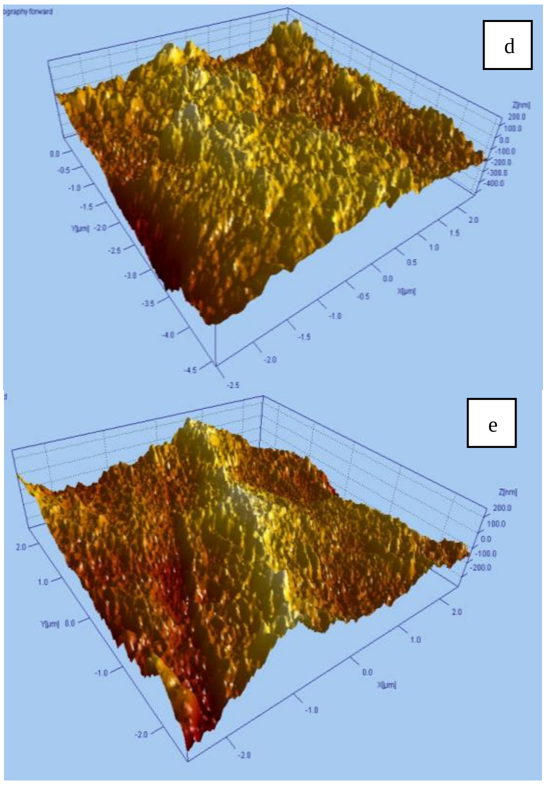


Figure 1. Surface topography of AA 6061 (a) Substrate (b) anodized at 15 V (c) anodized at 20 V (d) anodized at 25 V (e) anodized at 30 V

It appears from Fig. 1 (a) visible aluminum substrate surface topography is uneven. Not visible pores formed on the surface of the substrate. Only visible grains of non-homogeneous size. While in Fig. 1 (b) which is given a potential of 15 V, although the surface formed after the anodizing process has a tendency to have the same topography with substrate but began to appear in some parts of the surface pores as indicated by the red arrow. The increase in potential as shown by Fig. 1 (c), (d) and (e) make the size of the pore formed on the surface of the oxide layer becomes more uniform, so that the surface layer of the film becomes more homogeneous, roughness will decrease significantly.

Potential	Ra (nm)	RMS (nm)
Substrate	3.95	4.98
15 V	3.64	4.75
20 V	3.32	4.9
15 V	3.64	4.75
30 V	3.02	4.39

Table 1. Surface roughness values obtained from the AFM test

From Tab. 1 it can be seen that the potential applied during anodizing process affects the value of surface roughness (Ra) and the root mean square (RMS). The higher the potential at the time of anodization then the surface roughness value will be smaller.

The appearance of the topography of the anodized aluminum surface in Fig. 1 (b), (c), (d) and (e) shows the rate of oxide layer formation at different speed. The grain size is formed after the anodizing process appears to begin to show the size of an increasingly homogeneous along with increased potential. The rate of formation of the oxide layer affects the nucleation process and the diffusion of atoms during growth of the oxide layer. At the rate of formation at low potential, the ability of Al and Ti atoms to move towards the substrate is low enough that the process of forming the oxide layer on the surface of the substrate. This will result in a layer that is formed virtually no difference to the substrate due to the low current density nucleation, it will form a large grain size. When the applied potential increases, the rate of formation of oxide lapisa will also increase because of the number of Al and Ti atoms are moving on the surface of the substrate is also increasing. This will result in the faster the nucleation process so that the grains that are formed will be more homogeneous in size. The film layer with high surface roughness with non-uniform grain size as indicated by the surface topography of the AFM results in Fig. 1 (b) is obtained at the low oxide layer formation rate. While for Fig.s 1 (c) to Fig. 1 (e) it appears that the surface topography begins to show uniform results obtained from the increased potential applied.

The real effect on stressing the corrosion resistance of AA 6061 anodizing results by using the titanium cathodes. The measurement results were plotted on Tafel diagram as shown in Fig. 2. The kinetic parameters were obtained as V_{corr}, β_a, β_c, R_p and I_{corr} shown in Tab. 2

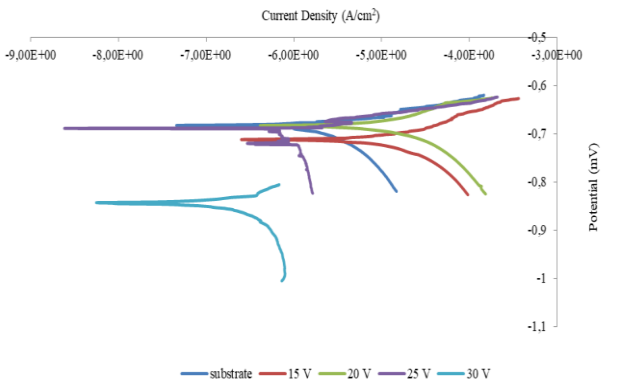


Figure 2. Anodic polarization curve AA 6061 which was anodized with different potential at 3.5% NaCl

Potential	E_{corr} (V)	β_a ($V.dec^{-1}$)	β_c ($V.dec^{-1}$)	R_p (Ω)	I_{corr} ($A.cm^{-2}$)
Substrate	1.031	125.580	39.3390	2.5183	5.165
15 V	1.02	23.54	14.8710	1.08	3.6641
20 V	1.018	102.72	64.810	1.039	16.666
15 V	1.009	28.1770	7.88240	0.0047	57.92
30 V	1.019	22.3070	15.2390	0.0743	52.86

Table 2. The data for the anodic film layer extracted film obtained from the tafel results in Fig. 2

Fig. 2 and Tab. 2 shows the results of potentiodynamic potential polarity of the coating film that is formed without and after the anodizing process. The density of corrosion current (I_{corr}), corrosion stress (E_{corr}) and polarization resistance (R_p) are used to evaluate the protective properties against corrosion in the anodized film coating. Icorr and E_{corr} values are derived from the potentiodynamic potential polarization curves by drawing a line parallel to the cathodic and anodic area lines so that the two parallel lines are intersected. The intersection of the line parallel to the Y axis is E_{corr} and the intersection of the x-axis line is I_{corr}. While the value of R_p obtained from equation (1) by β_a and β_c are anodic and cathodic Tafel slope.

In addition, Tab. 2 also shows the values of β_a and β_c. β_a and β_c are expressing the slope of the extrapolated linear line on the polarization curve. β_a shows the kinetics of an anodic reaction and β_c denotes the kinetics of cathodic reactions. This means that if the value of β_c is lower than β_a then the anodic reaction is greater than the cathodic reaction so that the metal will be more easily corroded because the current density is small. From Tab. 2 we find that the value of all β_a is much larger than its β_c value, this means that the anodizing result by using titanium cathode is actually corroded but the existing corrosion product is a passive layer formed as an anodizing product which precisely protects the aluminum metal against exposure of the environment.

The intersection of parallel lines on the curve can be drawn X axis value. Value on the X axis is the value of I_{corr}. I_{corr} value is one of the important value in determining corrosion rate because I_{corr} value will be multiplied by equivalent weight and divided by its density to get corrosion rate [Cheng 2015]. Significant changes in the polarization curve are seen at a potential of 20 V to 25 V with an increase of I_{corr} from 16.66 $A.cm^{-2}$ to 57.92 $A.cm^{-2}$. This indicates an increase in the formation of corrosion protection for the anodized film coating compared to the unanodized film layer. It can be said also that the layers formed after the anodizing process show a more positive corrosion value and lower corrosion current density when compared with unanodized substrates.

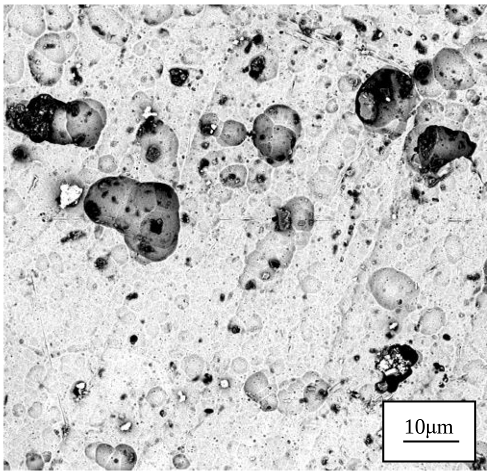


Figure 3. Substrate of AA 6061

The unanodized specimen surface is shown in Fig. 3. It appears that the surface has an uneven contour that is characterized by a large pit with a depth varying in size and form on the surface. It can also be observed that the distribution of pitting is not concentrated in one part only, but is evenly spread over the entire surface.

Fig. 4 shows the pitting occurring after anodizing results uponproviding potential variation. It appears in Fig. 4 (a) that pits are formed with a significantly large and deep sizes. The oxide film also totally removed from the surface of aluminium. Fig. 4 (b), after 20 V is applied in the anodizing process, showed a decrease in extent and depth of the pits formed after being exposed to a solution of 5% Sodium chloride. A porous form of the pit, as shown in Fig. 3 (c) reveals that the increase in potential gives a significant influence on the shape and depth of the pit that is formed. The size of the pit is significantly reduced in Fig. 4 (d).

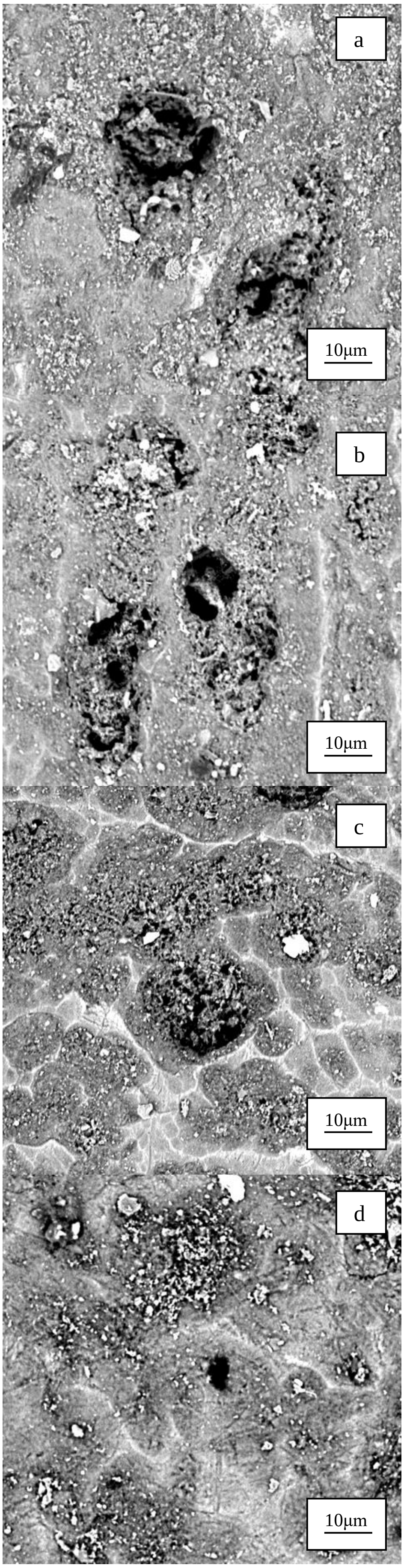


Figure 4. Pitting formation in different potential (a) 15 V (b) 20 V (c) 25 V (d) 30 V

Pitting formation is one of the most devastating forms of corrosion [Amin 2010]. Often it is difficult to detect the pit because of its small size and because the pits are often covered with corrosion results. So it is quite difficult to quantitatively measure and compare the rate of formation of the pits due to diverse depth and number of the pits that may occur in the same condition. The formation of the pit is also difficult to predict with laboratory tests.

Usually a pit develops in the direction of gravity. Most of the pits grow downward from the horizontal surface. Smaller number starts to form on vertical surfaces and pits rarely grow up from the bottom of the horizontal surface.

Pitting corrosion is a unique type of anode reaction [Stergioudi 2015]. It is a process called autocatalysis. Namely, the process of corrosion is created by generating conditions that encourage and are necessary for the sustainable pit activity. In this study, the results of the anodizing performed using a sodium chloride solution. Rapid discontinuation occurred in the pit, while the reduction of oxygen occurred on the surface nearby as reported before. This process begins and develops its own.

Rapid reduction of metal in the pit tends to produce an excess of positive charge in this area, which leads to the migration of chloride ions to maintain the neutrality of the electron [Lin 1981, Urquidi 1985]. Thus, in the pit there is a high concentration of sodium chloride and as a result of hydrolysis of the high concentration of hydrogen ions. Both hydrogen and chloride ions speed up the pit process over time. Because the solubility of oxygen in the solution concentrate is zero, there is no reduction of oxygen in the pit. Oxygen reduction at the cathode surface that is adjacent to the pit tends to suppress corrosion. In that sense, the pit protects other parts of the metal surface.

Gravitational effects mentioned earlier are a direct result of the nature autocatalytic pit formation. Because the solid solution is concentrated in the pits necessary for sustainable activities, it is most stable. When the pits develop in the direction of gravity. Also, pits are generally started on the top surface of the specimen because chloride ions are more easily maintained in this condition. From a practical standpoint, most of the failures are caused by the pit formation containing chloride ions. Chloride exists at various levels in most water and solutions made of water.

The mechanism for the formation of the pits by chloride can be explained by the tendency of formation of acid chlorides and the power of free acid. Oxidation of chloride ions in pits reduces the level of aggressiveness.

In general it can be said that the surface roughness that occurs during the anodizing process will reduce the lifetime and corrosion resistance. Thus reducing the amount of surface roughness formed on the oxide layer is assumed to increase the lifetime of the anodizing results because anodizing process is the only electrochemical process in aluminum that has a long lifetime with significant economic advantages to cost and operational cost savings, ease of care because it is not easy to be worn and worn out as well easy to clean, allowing to maintain metal appearance, and is a very effective process for health tools though. This corresponded to a study conducted by Shahzad et.al. which states that the fatigue life increased with decreasing surface roughness [Shahzad 2010].

4 CONCLUSIONS

This study examined the relationship between topography and corrosion resistance of AA 6061 after anodized in a mixture electrolyte solution of phosporic acid and oxalic acid. By using this process then along with increasing the potential will get the surface topography more uniform. The higher the potential given to the anodizing process, the smaller the RMS value as indicated on the RMS value for the lowest potential of 4.75 and for the highest potential decreased by 7.5%. Corrosion resistance was tested by the method of tafel and immersed test also showed an increase. Layer formed after the anodizing process is able to reduce the current density when compared with the substrate at 41.26 A.cm^{-2}. The use of titanium as cathode shows that this material is capable of enhancing the lifetime and beneficial course of the anodizing process. However, it is proved that the possibilities and the highest economy of aluminum anodizing are connected with its ability to withstand the rate of corrosion with increasingly low surface roughness after anodizing process.

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