

Military Type III Anodizing: The Optimal Limit Within Hardening Process of Aluminium Alloy in a Near Zero Temperature

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ABSTRACT

Hard anodization was a method that can enhance aluminium alloy surface characteristics by growing an aluminum anodic oxide (AAO) film on its surface. This method was very applicable to obtain a thick and hard coating. This process was carried out at galvanostatic-potentiostatic mode at high current densities ($j = 4.2 \text{ A/dm}^2$), high target voltages ($V_t = 30\text{--}60 \text{ V}$) and low electrolyte temperature. Two sulfuric acid electrolytes were compared, the first solution was sulfuric acid 11% vol., the second one was sulfuric acid 11% vol. plus oxalic acid 1% wt, both of them were conditioned at $<5^\circ\text{C}$. The maximum AAO film thickness and hardness obtained was $110.01 \mu\text{m}$ and 400 HV. The increase of target voltage was directly proportional to the increase in thickness and hardness of the AAO film. The results of this study could be synergized with the manufacturing process of aluminum alloy-based (Al6061) components at the product finishing stage. The logarithmic regression in the function of target voltage could be used to estimate film thickness and hardness of the films.

Keywords: Al6061, Hard Anodizing, Aluminium Anodic Oxide (AAO), Micro Vickers Hardness.

1. INTRODUCTION

Aluminum alloys have been widely used as a main material in the engineering world. Aluminum is a low cost, reliable and light weight material that has a high strength-to-weight ratio. However, aluminum alloys have problems of surface damage due to their softness. These deficiencies become an obstacle to wider application and advances of surface treatment are needed to overcome these problems [1].

Aluminium alloy surface characteristics can be enhanced electrochemically by anodization to grow a metal oxide on its surface. The layer formed is called the aluminum anodic oxide (AAO) films. This anodic coating can be produced on aluminium alloys by using a wide variety of electrolytes with AC, DC, or a combination of both electrical current modes [2].

The coating industry categorizes AAO films into several types based on their mechanical properties and anodization process. Although there are editorial differences in standards such as ASTM B 580, MILITARY-A-8625F, etc., in general the AAO films are

categorized into three types of anodization. Type I anodization for low current density (about $0.3 - 1.5 \text{ A/dm}^2$) chromic acid based coatings and $1 \mu\text{m}$ layer thickness. Type II anodization for sulfuric acid-based coatings with higher current densities (about $1.0 - 2.0 \text{ A/dm}^2$) and $3\text{--}18 \mu\text{m}$ thickness. Type III anodization for sulfuric acid-based coatings with high current densities (about $1.5 - 3.0 \text{ A/dm}^2$) and thickness above $25 \mu\text{m}$ [3][4].

Type III anodizing in many scientific journals and engineering books is more popular called hard anodizing. Meanwhile, type I and II anodization is called mild anodization. Components that were treated with hard anodizing were generally components that really need wear or abrasion resistance on their surface; for example pistons, cylinders and gears. Hard anodizing coating is a surface treatment technique that optimally improves the surface resistance of aluminum when compared to mild anodization [5]. Hard anodizing can also increase the tribology performances of components due to the growth of a hard and compact oxide layer. Hard anodizing finds its large application in advanced structural engineering sectors as automotive, motorsport, aerospace and military [6].

The hard anodizing coating method was very applicable to obtain thick ($> 50\mu\text{m}$) and hard ($>250\text{ HV}$) AAO films with fast forming duration. This surface treatment method is an attractive method because it has a high-speed coating rate ($0.83 - 1.67\ \mu\text{m}/\text{min}$) [7]. This AAO growth process was carried out at a high current density and electrolyte temperature which is conditioned close to zero degrees celsius. The use of electrolytes at very low temperatures was a key factor for producing a hard surface coating [8].

Research by Chu *et al.* and Schwirn *et al.* showed that power supply setup with the galvanostatic-potentiostatic mode at high current densities ($j = 2.5 - 100\ \text{A}/\text{dm}^2$) and high target voltages ($V_t = 27 - 80\ \text{V}$) at $1.8\ \text{M}\ \text{H}_2\text{SO}_4$ sulfuric acid electrolyte in low temperatures (1°C) resulted an AAO film with a thickness in the range of $11.5 - 300\ \mu\text{m}$ using pure aluminum specimens (99.99%). This approach was technically quite simple and cost-effective [9][10]. Bensalah *et al.* compared the effect of anodization parameters on the AAO growing rate in AA1050 aluminum alloy specimens using a doehlert experimental design [11]. The optimization study showed that the optimum anodization conditions ($T_{\text{electrolyte}} \leq 5.7\ ^\circ\text{C}$, $j = 3\ \text{A}/\text{dm}^2$, $C_{\text{sulfur}} = 1.4\ \text{M}$) resulted in a high AAO growing rate ($0.86\ \mu\text{m}/\text{min}$) and a high films density ($3.12\ \text{g}/\text{cm}^2$). Wu *et al.* also found that two-step anodization could effectively widen the applications of AAO films, either as high-precision nanoporous templates or as ultrathin functional materials [12].

This study was a surface treatment that refers to the galvanostatic-potentiostatic mode by Chu *et al.* and Schwirn *et al.* as an electrical setup during the anodization process. Anodization parameters, especially current density and electrolyte temperature, adapted the optimization research from Bensalah *et al.* Research on hard anodizing Al6061 aluminum alloy using galvanostatic - potentiostatic electrical mode is still not much done. Aluminum alloy 6xxx series was one of the recommended aluminum alloys that were suitable for use as the parent metal to produce a tough and corrosion-resistant coating [13].

All aluminium alloys do not accept hard anodize coatings equally well. Hard anodize coatings on alloys with high copper or silicon content tends to be porous and not very hard. This study used a sulfuric acid based electrolyte because sulfuric acid was an electrolyte that can be used in almost all alloys with a copper content limit not exceeding 5.0% and silicon not exceeding 7.0% [13]. In addition, this research also tries to optimize the mechanical properties of the coating by adding variations of oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ into the electrolyte solution [14].

2. METHOD

The specimen used in this study was a cylindrical aluminum alloy Al061-T0 (no heat-treatment) with a

length of 25 mm and a diameter of 10 mm. The AAO film was grown only on the upper surface of the cylinder. Markers and non-sticky tape were used to chemically and electrically insulate the side and bottom surfaces of the cylinder. The upper surface of the specimen is smoothed with sandpaper (100-2000 grit size). Then chemically etched with 5% NaOH solution at room temperature for two minutes and rinsed with distilled water.

The heat exchanger and agitation systems are combined into one in this research. Circulation in the heat exchange process is also used to maintain the solubility of ions (Al^{3+} , O^{2-}) so that the electrolyte solution remains homogeneous. The circulating temperature of the solution was kept low $<5\ ^\circ\text{C}$ during the anodization process. Electrical system uses a two-step electricity, the condition of a constant current (galvanostatic) and constant voltage (potensiostatic).

The schematic diagram of the tool is shown in Fig. 1. The anodization process is an exothermic reaction which causes the surface of the coating to heat up and heat up the electrolyte solution. During the coating process, the electrolyte solution is circulated to the heat exchanger system. Heat is dissipated from the copper coil to the cooling medium. The cooled electrolyte then returns to the electrolyte bath.

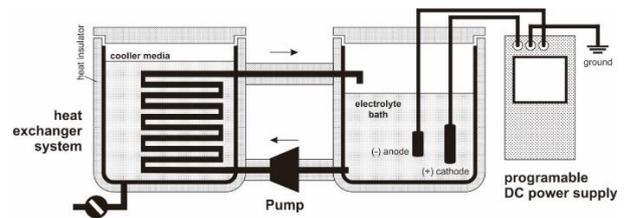


Figure 1 Schematic for hard anodizing surface treatment

The electrolyte solution is divided into two variations. The first variation (1) was sulfuric acid 11% vol. Dilution is carried out by slowly dissolving 224.5 mL of sulfuric acid 98% vol into 2 L of distilled water. The second variation (2) was sulfuric acid 11% vol plus oxalic acid 1% wt. Dilution is carried out by slowly dissolving 224.5 mL of sulfuric acid 98% vol into 2 L of distilled water plus 20 grams of oxalic acid powder.

The anodization process begins with a galvanostatic condition at $4.2\ \text{A}/\text{dm}^2$ then switch to potentiostatic when it reaches the target voltage V_t and then maintained until the current density decreased to $1.0\ \text{A}/\text{dm}^2$. The target voltage consists of three variations 30, 40 and 60 Volts. Voltage, current and electrolyte temperature profiles were observed every minute using voltmeter, ammeter and thermometer.

The surface morphologies of the hard-anodized specimen at different target voltages were observed by Optical Microscopy (OM). The cross section of developed oxide film was observed by Optical

Microscopy to obtain the coating thickness [15]. The micro-harnesses of the hard-anodized coating were observed with Micro Vickers method. The surface defect were observed by FE-SEM.

3. RESULT AND DISCUSSION

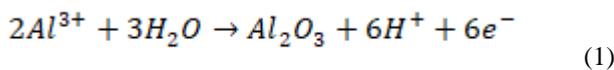
3.1. Aluminium Alloy Al6061-T0 Composition.

Table 1. Alloy composition wt% of Al 6061 T0 [16]

Component	Wt. %	Component	Wt. %	Component	Wt. %
Al	95.8 – 98.6	Mg	0.8 – 1.2	Si	0.4 – 0.8
Cr	0.04 – 0.35	Mn	Max 0.15	Ti	Max 0.15
Cu	0.15 – 0.4	Fe	0.7	Zn	Max 0.25

3.2. Ions Transport Mechanism

Electrochemical anodization of Al6061-T0 aluminium alloys to form thick oxide films has been carried out. Anodization was an electro-chemical process which can be described as a closed electrical circuit. Metal oxide formation reactions can occur through dissolution of anodic metals to form suitable cations followed by reactions between metal cations and ionic oxygen [17]. The electric charge carriers that flowing through the AAO film were Al^{3+} and O_2^- . The final reaction of aluminum oxidation:



The composition limits for the specimen Al6061-T0 aluminium alloys in wt.% are listed in Table 1. The various alloying elements are present in the aluminium substrate as solid solutions, or second phases, such as zones, precipitates, or intermetallic compounds of various shapes, sizes and compositions. It plays role in AAO film growth and microstructure during anodization.

3.3. Voltage and Temperature Profile

The electrical profile of the target voltage 40V was shown in Fig. 2a. The use of 11% vol sulfuric acid electrolyte with the addition of 1% oxalic acid had a higher current density profile than without addition. Fig. 2b shows that the use of 11% vol sulfuric acid electrolyte with the addition of 1% oxalic acid can reduce the electrolyte temperature profile during the anodization. Temperature reduction optimizes electrical processes. The temperature reduction optimizes the electrical process and increases the reaction formation of Al_2O_3 then speeds up the AAO film growth process, resulting in a thicker film.

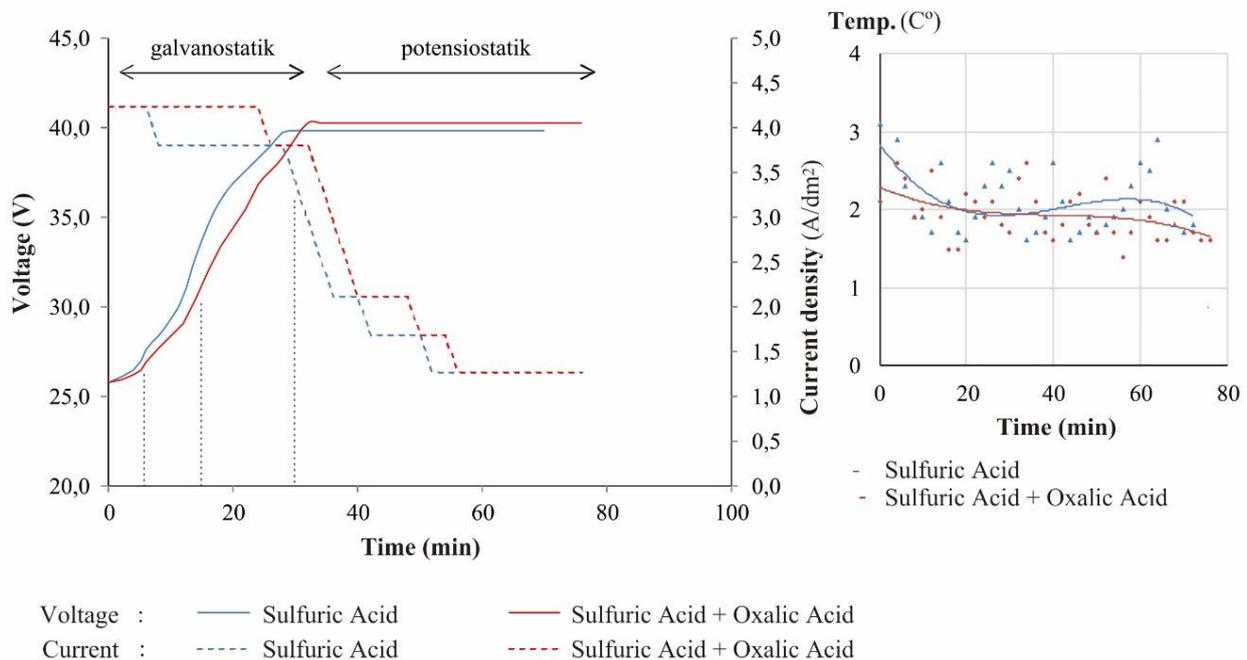


Figure 2 Electrical profile (a) and temperature profile (b) during the hard anodizing process at the target voltage $V_t = 40 V$

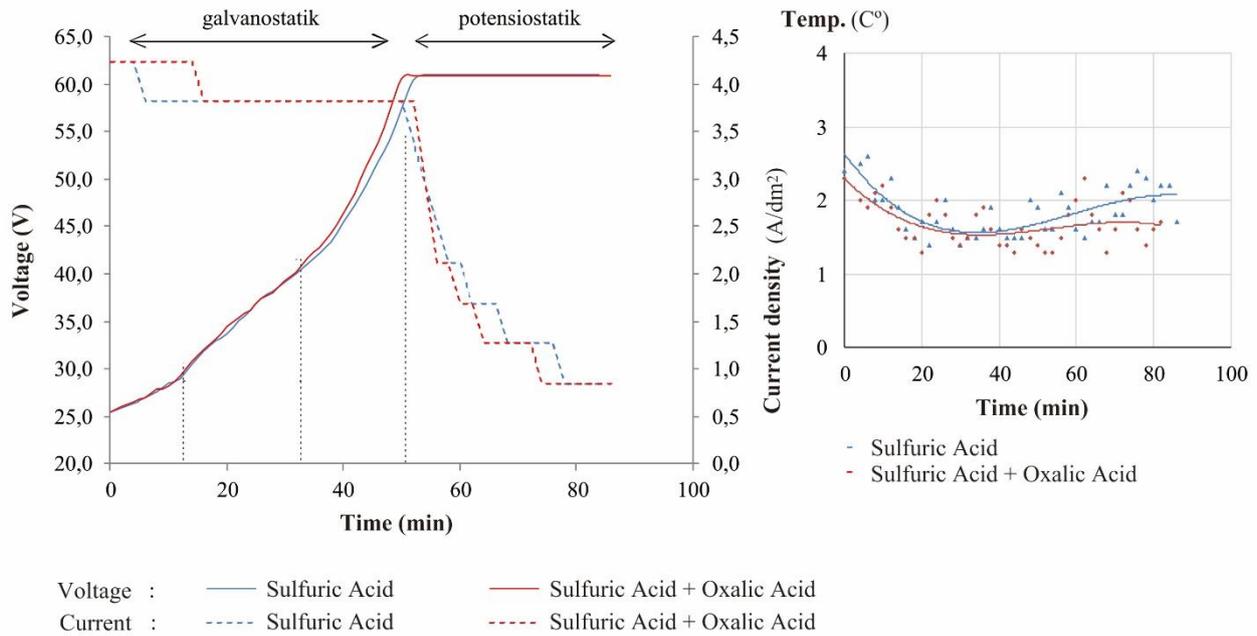


Figure 3 Electrical profile (a) and temperature profile (b) during the hard anodizing process at the target voltage $V_t = 60\text{ V}$

There was a slight difference in the electrical profile in Fig. 3 (a) on the target voltage parameter $V_t = 60\text{ V}$. The current density in the 11% vol sulfuric acid electrolyte with the addition of 1% wt oxalic acid (red stripe) at the 5 to 55 minute was higher than the current density in the 11% vol sulfuric acid electrolyte (blue stripe), However, from the 55 minute till the end of the anodization, the current density in the 11% vol sulfuric acid electrolyte with the addition of 1% wt oxalic acid (red stripe) was lower than the current density at anodization in the 11% vol sulfuric acid electrolyte (blue stripe line).

3.4. AAO Films Growth

The relationship between the target voltage and thickness in Fig. 4 shows that the variation of 1% wt addition of oxalic acid was good for use at target voltages below 50V. The use of target voltage above 50V results in reduction Δ in film thickness. The use of voltages above 50V was more suitable for variations of the 11% vol sulfuric acid electrolyte without the addition of 1% wt oxalic acid.

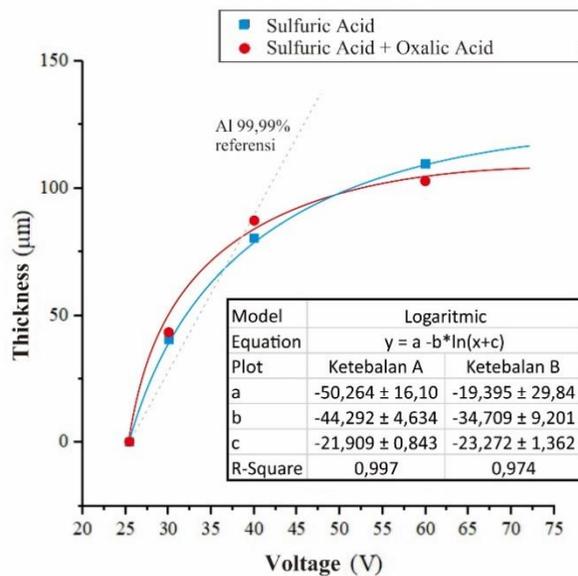


Figure 4 Plot V_t target voltage vs thickness

3.5. The Micro-Hardness of AAO Films

The AAO film increases its hardness significantly as the target voltage increases. The relationship of target voltage with the thickness and hardness was shown in Fig. 6. The diagram with a solid color bar shows the

hardness value, while the shaded colored bars show the thickness value. The blue color shows specimens in 11% vol H_2SO_4 sulfuric acid electrolyte, while the red color shows specimens in 11% vol H_2SO_4 sulfuric acid electrolyte with the addition of 1% wt $H_2C_2O_4$ oxalic acid.

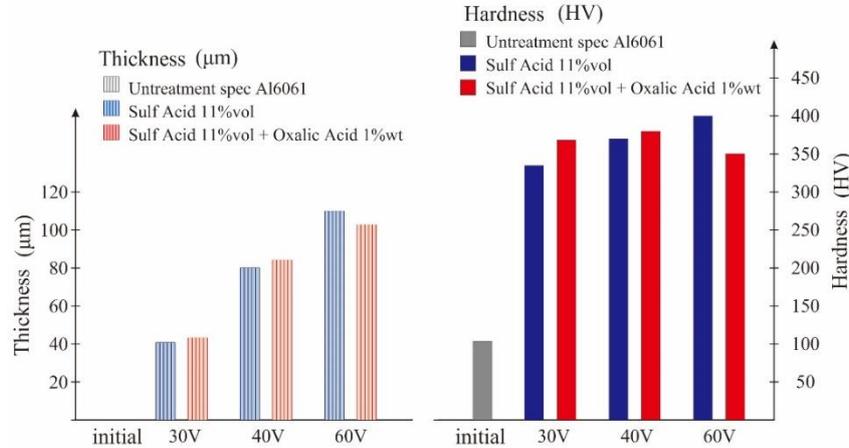


Figure 6 Chart of AAO Film thickness and hardness in different electrolyte solutions and target voltages.

The initial voltage (25V) in Fig. 6 was the initial electrical breakdown voltage. In the initial voltage condition, it is assumed that the AAO film has not been formed and the hardness value same as the initial specimen hardness value 103.5 HV. The thickness and hardness of the films were directly proportional to the increase in target voltage V_t .

micron on the surface of the layer. When compared with the anodizing in variations without the addition of oxalic acid in Figure 5(a), at the same target voltage parameter. No cracks were found on the 1 micron scale on the films surface. This FE-SEM image confirms that the stress release on anodization with sulfuric acid variation is better than that with the addition of oxalic acid.

Films optimization does not occur at target voltage 60V. In fact, this optimization was resulting lower thickness and hardness than the variation without the addition of oxalic acid. This phenomenon may occur because the addition of oxalic acid increases the current density profile and results in too high stress on the oxide columns, especially in the target voltage 60V. Observation of FE-SEM images with a magnification of 100,000x in Figure 5(b) showed cracks at a scale of 1

The films properties in many heat treated aluminum alloys are seriously affected by intermetallics, microstructural and compositional inhomogeneities as mentioned in section 3.1. Furthermore, distorted distributions of electric field are possible and they can lead to inhomogeneous oxide growths. Through the optimization of electrolyte, current density, voltage and other variables a good compromise between hardness, compactness and low defectiveness can be achieved.

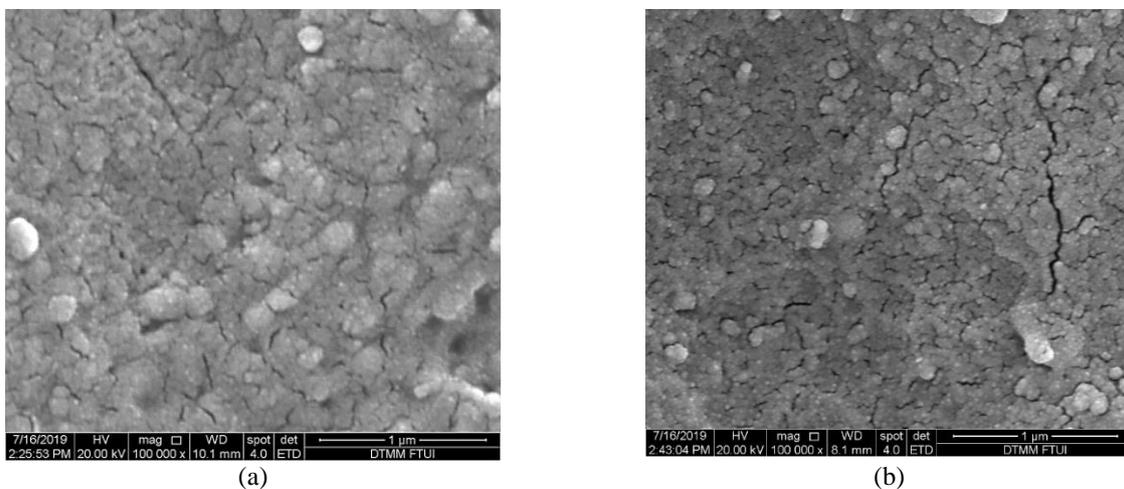


Figure 5 FE-SEM images of AAO films $V_t = 60V$ with 100.000 magnification. (a) sulfuric acid H_2SO_4 11%vol electrolyte. (b) sulfuric acid H_2SO_4 11% vol + oxalic acid $H_2C_2O_4$ 1% wt electrolyte.

4. CONCLUSION

The characteristics of AAO films were influenced by the type of aluminium alloys and the anodizing conditions. The films thickness vary with the anodizing parameters. The optimum anodizing target voltage for each electrolyte are 60V for 11% vol H₂SO₄ sulfuric acid electrolyte and 40V in 11% vol H₂SO₄ sulfuric acid electrolyte with the addition of 1% wt H₂C₂O₄ oxalic acid. The maximum film thickness in this study was 110.01 μm which was produced using 11% vol sulfuric acid electrolyte with current density 4.2 A/dm², target voltage 60V and electrolyte temperature ~2°C.

The target voltage variations (30V, 40V and 60V) was directly proportional to the increase in thickness and hardness. Increasing the target voltage of 30V, 40V and 60V at the variation of the sulfuric acid electrolyte of 11% vol produced AAO films with a hardness of 334.8 HV; 370.0 HV and 400.0 HV. While increasing the target voltage of 30V, 40V and 60V in the electrolyte with the addition of 1% wt oxalic acid produces films with a hardness of 368.5 HV; 380.0 HV and 350.4 HV. From films thickness and hardness of all variable in this study, the anodized layer meets the standard specification MIL-A-8625F and ASTM B 580.

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