Characterization of Tartaric-Sulphuric Acid Anodized 2024-T3 Aluminium Alloys with Anodizing Potential Variation

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Abstract. The influence of anodizing potential on corrosion resistance, coating weight, and coating thickness of AA 2024-T3 aluminium alloy anodized in tartaric-sulphuric acid (TSA) has been investigated. Specimens were anodized in TSA bath then sealed in boiling water bath. Anodizing was performed with potential variations of 11, 13, 15, 17, 19, and 21 volt (V). Corrosion resistance test was carried out by 96 hours salt spray test and potentiodynamic polarization. Coating weight was determined by gravimetric method and coating thickness was determined by metallographic method. Salt spray test results showed that anodizing potential did not affect corrosion resistance. Corrosion potential has the same value with pitting potential for all specimens. Corrosion potential increases with increasing anodizing potential from 11 V until 19 V and then decreases at 21 V anodizing potential. Corrosion current was not affected by anodizing potential. Coating weight and coating thickness increases with increasing anodizing potential.

Keywords: Anodizing, Al 2024-T3 alloy, Tartaric-sulphuric

1. Introduction

Aluminum is the ideal material for aircraft manufacturing industry because of lightweight, strong, and flexible. Aluminum composes 75-80% of modern aircraft [1]. Pure aluminum has very low yield strength (7-11 MPa). Therefore, alloying is done to increase the strength of aluminum [2].

2024 aluminum alloy is one of the most widely used alloys for aircraft materials. 2024 aluminum alloy is used on body surface, wings, body structure, and wing support. However, 2024 aluminum alloys are susceptible to atmospheric corrosion especially in industrial and marine environments [3].

Anodizing and sealing can be performed on aluminum alloys to improve corrosion resistance [4]. Anodizing is a coating process by changing the surface of aluminum or its alloys into porous aluminum oxide. Anodizing is done by making the aluminum to be coated as anode on the electrolysis cell [5]. To obtain optimal corrosion resistance, sealing is done on anodized aluminum. Sealing is converting anodized aluminum oxide to boehmite [6].

Chromic acid anodizing (CAA) is one type of anodizing process used to improve the corrosion resistance of aluminum alloys [7]. Chromic acid is also used in the process of CAA aluminum sealing to produce optimum corrosion resistance [8,9]. However, the use of chromic acid containing Cr (VI) ions can be detrimental to health and the environment [10].
Tartaric-sulfuric acid can be a more eco-friendly alternative to electrolyte to replace chromic acid in anodizing and boiling water for sealing \cite{11-16}. The purpose of this study was to study the effect of anodizing potential on corrosion resistance, coating weight, and thickness of aluminum alloy 2024-T3 coating that was anodized by tartaric acid sulphate.

2. Experimental

The chemical composition of 2024-T3 aluminum alloys used in this experiment is shown in Table 1. Prior to the anodizing, the specimens were cleaned using methyl ethyl ketone (MEK), dried with air, and soaked in a Turco 4215 NC solution for 15 minutes. Then, the specimen was etched by Aluminetch N2 alkaline solutions for 1 minute and last was soaked in a solution of Ardrox 295GD for 10 minutes. Each immersion stage is followed by a rinsing stage using demineralized water.

Anodizing was carried out in a solution containing 87 grams / liter tartaric acid and 44 grams / liter sulfuric acid at 37 °C. At the beginning of the anodizing process, the potential is increased within 5 minutes and is maintained for 20 minutes. Anodizing is carried out with potential 11, 13, 15, 17, 19, and 21 V. The cathode used in this process is stainless steel. Stirring is done during the anodizing process. After the anodizing process, the specimens were rinsed for 5 minutes immediately. Sealing is done in boiling water for 50 minutes after the specimen is rinsed. Finally, the specimens are air dried and ready to be tested.

Anodizing using chromic acid was also performed as a comparison. The content of chromic acid in the solution used for this anodizing is 46 g / L. The temperature of the solution is kept at 40 °C. Anodizing is performed with 40 V anodizing potential for 40 minutes.

Table 1 Chemical Composition of Alloy 2024-T3 Composition Elements (wt%)

| Element   | Composition (wt%) |
|-----------|-------------------|
| Si        | 0,5               |
| Fe        | 0,5               |
| Cu        | 3,8-4,9           |
| Mn        | 0,3-0,9           |
| Mg        | 1,2-1,8           |
| Cr        | 0,1               |
| Zn        | 0,25              |
| Zr + Ti   | 0,2               |
| Ti        | 0,15              |
| Others    | 0,15              |
| Al        | Balance           |

The corrosion resistance was tested by salt spray test and potentiodynamic polarization. The salt spray test was carried out for 96 hours using a 5 wt% NaCl solution. The polarization was performed on 1 cm² specimens, Ag / AgCl electrode was used as reference, and platinum as opposing electrode. The test was performed using a Gamry Reference 600 potentiostat in room temperature with a 3 wt% NaCl solution. Potentiodynamic polarization is performed with a potential rate of change of 0.167 mV / second from -200 mV versus open circuit potential (OCP) to breakdown potential.

The coating weight is tested by looking at the difference in specimen weight before and after immersion in a solution containing phosphoric acid and chromic acid. Coating thickness was observed with an optical microscope at five points. Morphological observations and compositions were performed by Scanning Electron Microscope / Energy Dispersive Spectroscopy (SEM-EDS). XRD testing was conducted at Hydrogeology and Hydro geochemistry Laboratory of Mining Engineering Institut Teknologi Bandung.
3. Results and discussion

3.1 Salt Spray Test

Salt spray test result showed that no association between the anodizing potential with corrosion resistance. The anodized specimens using tartaric acid (TSAA) with anodizing potential of 11 V, 13 V, and 17 V did not experience pitting corrosion. TSAA specimens with anodizing potentials of 15 V, 19 V, and 21 V experienced pitting corrosion with varying number of holes. The relation between the amounts of holes to the anodizing potential is given in Figure 1. Specimens without anodizing process suffered severe corrosion. CAA specimens did not suffer pitting corrosion.

3.2 Potentiodynamic Polarization

![Potentiodynamic Polarization Curve](image-url)
Figure 2 shows polarization curves of potentiodynamic polarization test on specimens with various treatments. The $E_{\text{corr}}$ has the same value as $E_{\text{pit}}$ for all specimens because a sudden increase of current occurs when the $E_{\text{corr}}$ is reached. The $E_{\text{corr}}$ increased with increasing anodizing potential from 11 V to 19 V and then decreased at 21 V anodizing potential. This indicated that the corrosion resistance was increasing with increasing of anodizing potential. The value of $I_{\text{corr}}$ indicates no relationship between the anodizing potential and corrosion resistance. Table 2 shows the corrosion parameters obtained from the polarization curve.

| Treatment | $I_{\text{corr}}$ (A) | $E_{\text{corr}} = E_{\text{pit}}$ (mV vs. Ag/AgCl) |
|-----------|-----------------|---------------------|
| NA        | 6.29x10$^{-07}$ | -634                |
| CAA 40 V  | 1.26x10$^{-07}$ | -555                |
| TSAA 11 V | 3.32x10$^{-08}$ | -721                |
| TSAA 13 V | 4.85x10$^{-08}$ | -672                |
| TSAA 15 V | 2.91x10$^{-09}$ | -637                |
| TSAA 17 V | 2.99x10$^{-08}$ | -556                |
| TSAA 19 V | 1.52x10$^{-08}$ | -311                |
| TSAA 21 V | 1.79x10$^{-06}$ | -636                |

The largest $E_{\text{pit}}$ is owned by TSAA specimen with 19 V anodizing potential that is -311 mV vs. Ag/AgCl. The lowest $E_{\text{pit}}$ is owned by TSAA specimen with 11 V anodizing potential that is -721 mV vs. Ag/AgCl. The specimens were anodized by TSAA with a potential of 17 V, 19 V, and anodized specimens with CAA had larger $E_{\text{pit}}$ when compared to untreated specimens. When compared to anodized specimens using CAA, only the specimens that were anodized by TSAA with potential 19 V had a larger $E_{\text{pit}}$. $E_{\text{pit}}$ with a large value indicates good corrosion resistance.

The smallest $I_{\text{corr}}$ is owned by TSAA specimens with anodizing potential of 15 V that is 2.91x10-09 A. The largest $I_{\text{corr}}$ is owned by a TSAA specimen with an anodizing potential of 21 V of 1.79x10-6 A. When compared to untreated specimens, only TSAA specimens with potential 21 V have larger $I_{\text{corr}}$. It shows that good anodizing and sealing can increase the value of the $I_{\text{corr}}$. When compared to CAA specimens, only TSAA specimens with a 21 V anodizing potential have larger $I_{\text{corr}}$. Small values of $I_{\text{corr}}$ indicate good corrosion resistance.

### 3.3 Coating Weight

Figure 3 shows coating weight of the anodized specimens with various treatments. The highest coating weight is owned by TSAA 2024-T3 aluminum with anodized potential of 21 V. The lowest layer weight is owned by TSAA 2024-T3 aluminum with anodizing potential of 11 V. The weight of the anodized and sealing oxide coating will increase as the anodizing potential increases.
3.4 Coating Thickness

Figure 4 shows the thickness of the oxide layer on aluminum 2024-T3 with various treatments. The largest layer thickness is owned by TSAA 2024-T3 aluminum with anodized potential of 21 V. The lowest layer thickness is owned by TSAA 2024-T3 aluminum with anodized potential of 11 V. As comparison, the 2024-T3 aluminum that is anodized with chromic acid has a coating thickness of 3.618 mm. The thickness of the anodized specimens will increase as the anodizing potential increases.

3.5 Morphology and Composition

SEM photographs are shown in Figure 5 (a and b). Prior to the salt spray test, specimens without anodizing treatment have a small, densely circular surface structure with no pores between the circles. On chromic acid anodized specimen the circle structure is no longer visible. Additionally, the CAA processed specimen also highlighted the texture of the existing scratches on specimens. In the TSAA results specimen, the circles structure is still visible in a small area. The structure of the circle is noticeable again because aluminum oxides covers the structure. After the salt spray test, surface of the untreated specimen has a clump structure on most surfaces. The clumps are aluminum oxides of
corrosion results. In addition, cracks also appear on the surface of the specimen. Significant holes are also seen in SEM photo images on untreated specimens. The filament holes, cracks, and corrosion are seen in specimens of TSAA 15 V. Holes and cracks in specimens of TSAA 15 V are smaller than specimens that are not treated. The filiform corrosion is seen in some parts of this specimen. The lump structure does not appear in specimens of TSAA 15 V. This indicates TSAA 15 V and sealing with boiling water may increase the corrosion resistance of the aluminum alloy 2024-T3. The holes are visible in CAA results specimens. The hole in CAA yield specimens is smaller than in non-treated specimens. The lump structure is not visible in CAA results specimens.

Observations were also carried out on the thick part of anodized specimen. Structural observations were performed with SEM while the observation of the content was done with EDS. Observation using SEM shows two different layers. At the bottom is seen the base of the base metal while the upper part looks the oxide layer structure of anodized and sealing. The structure of the fibers is visible in the anodized layer of the product using chromic acid and using tartaric sulfate acids. The content of the chromate acid anodized layer is 38.82% aluminum atoms and 61.18% atoms of oxygen. TSAA layer content is 31.70% aluminum atoms and 68.30% atoms of oxygen. The comparison of aluminum atoms with oxygen at the oxide layer of chromate acid anodized acid obtained a value of about 2: 3. The comparison of aluminum atoms with oxygen at the oxide layer of TSAA yields a value of about 1: 2. The anodized oxide layer is Al2O3. At Al2O3, the ratio of aluminum atoms with oxygen atoms is 2: 3. The difference in the ratio of aluminum atoms to oxygen at the TSAA oxide layer can be caused by the residual acid contained in the oxide layer.\[17\]. XRD is performed to determine the phase formed from anodizing and sealing processes. However, the results of this test did not show the phase of the anodized and sealing lining. This can be due to the thickness of the anodized and sealed layer of the sealing material.

Figure 5a Top view of SEM photographs results before salt spray test (a and c), after salt spray test (b and d), unanodized (a and b), TSAA 15 V (b and c)
4. Conclusions
The salt spray test showed that the anodizing potential using tartaric sulfate (TSAA) acid did not affect the corrosion resistance. The corrosion potential ($E_{\text{corr}}$) has the same value as the pitting potential ($E_{\text{pit}}$) for all specimens. The $E_{\text{corr}}$ increases with anodizing potential increase from 11 V to 19 V and then decreases at anodizing potential 21 V. The corrosion current ($I_{\text{corr}}$) is unaffected by anodizing potential. The weight of the coating and the thickness of the coating increases with the increasing of anodizing potential.

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Figure 5b Top view (e and f) and side view (g and h) of SEM photographs results before salt spray test (e and g), after salt spray test (f and h), TSAA 15 V (e and g), and CAA (f and h)
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