Effect of Potential on Corrosion Behavior of Tartaric-sulphuric Acid Anodized 7075 T6 Aluminum Alloys

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Abstract. Anodizing of aluminum alloy in tartaric-sulphuric acid (TSA) is studied as an alternative to replace chromic acid anodization (CAA) to obtain more environmentally-friendly process. Bare 7075 T6 aluminum alloy specimens were anodized in TSA and subsequently protected by boiled water sealing treatment. The TSA solution used contains 86.76 gpl tartaric acid and 44 gpl sulphuric acid at 37°C. Some specimens are anodized in CAA as comparison. In this research, the effect of anodization potential of 7075 T6 aluminum alloy in TSA on the thickness, weight, and corrosion resistance of anodize layer are studied. Corrosion resistance test was carried out by conducting salt spray test for 96 hours and corrosion potential and current density measurement using potentiostat. The morphology and chemical composition of the sealed anodize layer were evaluated by scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The results showed that the thickness and weight of the anodize layer increases as the anodization potential increases. The best corrosion resistance is achieved by 7075 T6 aluminum alloy specimen with potential anodization of 15 V.

1. Introduction

Aluminum alloys are widely used in the aerospace industry because of its strength, lightweight, and easy to shape. Typically, aluminum alloys are used on the wings and bodies of the aircraft. The two most widely used as aircraft components are the 2xxx and 7xxx series [1,2]. However, the aluminum alloy is known to have relatively poor corrosion resistance [3]. One common method used to improve the corrosion resistance of the aluminum alloys is anodization using an acidic electrolyte solution [2].

Nowadays, the anodizing process of aluminum alloys that are widely performed in the aircraft industry is anodizing by using chromic acid (CA) solution [4]. However, chromic acid is very toxic. Therefore, for anodizing process to be environmentally friendly, research has been done to replace chromic acid as an electrolyte solution in anodizing process [5]. Since 2002, anodizing of aluminum alloy in tartaric-sulphuric acid (TSA) electrolyte is developed to replace chromic acid solution [6]. Several studies on the use of TSA as an electrolyte solution in the anodizing process have been performed [7-9]. However, information on potential effects in anodizing processes using TSA solutions on aluminum alloy 7075 T6 is still limited. Therefore in this study the potential anodizing effect using tartaric-sulfate acid on coating thickness, coating weight and corrosion resistance on aluminum alloy 7075 T6 was performed. Anodization was also carried out using chromic acid solution as a comparison.
2. Material and Experimental

Aluminum alloy 7075 T6 was used in this study. The material was supplied by PT. Dirgantara Indonesia. The chemical composition of the alloy is shown in Table 1. The materials are prepared according to AIPS (Airbus Process Standard) 02-01-003 [10] into two different test specimen sizes. Weight measurement, coating thickness, potentiodynamic polarization, and SEM/EDS analysis using a sample size of 1´75´75 mm. Meanwhile, 1´80´125 mm specimens were prepared for salt spray testing.

| Table 1. Chemical composition of Al 7075-T6 (%wt). |
|----------|----------|----------|----------|----------|----------|----------|----------|
| Al       | Cr       | Cu       | Fe (max) | Mg       | Mn (max) | Si (max) | Ti (max) | Zn       | Others (max) |
| 87.1-91.4| 0.18-0.28| 1.2-2.0  | 0.5      | 2.1-2.9  | 0.3      | 0.4      | 0.2      | 5.1-6.1  | 0.15        |

The specimens are cleaned of dust, oil, ink, fingerprints, and other impurities that can reduce the effectiveness of the anodizing process. The cleaning process is done through several stages. The first stage is mechanical cleaning by rubbing the surface of the specimen with sanding sponges. The second stage is surface cleaning using an organic solvent by dipping the specimen into a methyl ethyl ketone (MEK) solution. The third stage is alkaline cleansing. This process is performed by immersing the specimen into a tank containing 30 - 60 gpl Turco 4215 NCLT solution for 15 minutes. Before the specimen is treated at a later stage, the specimen is rinsed in the flushing tank for 5 minutes. The fourth stage is aluminetching. The process is done by immersing the specimen into a solution containing 30- 40 gpl of aluminetch in 60°C for 1 minute. After aluminetching, the specimen was rinsed in the flushing tank for 2 minutes. The final stage is deoxidation. The process is carried out by immersing the specimen into the solution of Ardrox 295 GD in 30-40°C for 10 minutes. Then, rinse in the flushing tank for 3 minutes.

Anodization with tartaric-sulfuric acid was performed at 37°C for 26 min with tartaric acid concentration of 86.76 gpl and sulphate acid concentration of 44 gpl. The variation of the anodizing potential is 11, 13, 15, 17, 19, and 21 V. Meanwhile, some other specimens were anodized with chromic acid as comparison. The process was performed at 40°C for 40 minutes with a concentration of 46 gpl of chromic acid (CA). The anodizing potential for the process was 40 V. The anodizing process parameters using the CA solution are a common process applied to any of the components in the aerospace industry. After the anodizing process, the specimens were sealed in boiled water (96-100°C) for 50 minutes.

After sealing process, coating thickness was measured by optical microscope observation (ISO 1463). Coating weight measurement was carried out by gravimetric method (ISO 2106) [11]. Salt spray test was done based on ISO 9227. The salt spray test (SST) was performed in a salt spray chamber. Three specimens were used for every treatment. The specimens were sprayed continuously by 5% NaCl solution for 96 hours (4 days).

Potentiodynamic polarization testing was performed on a 1´10´10 mm specimen in a 3% NaCl solution at 25°C. The counter electrode used is platinum, while the reference electrode used is Ag/AgCl. Measurements were performed with a scan rate of 0.167 mV/s. SEM-EDS observation was performed on the cross-section of anodized specimens. Observation was also carried out on the specimen surface prior to and after salt spray test.

3. Results and Discussion

3.1. Effect of anodization potential to coating weight and thickness

The results of the thickness and weight measurements of the anodizing layer are presented in Table 2. Using tartaric-sulfuric acid solution, the average of the thickness and weight of the anodizing layer formed on Al 7075-T6 is increased with increasing anodizing potential. This is in accordance with Faraday’s law stating that the coating thickness is proportional to the electric current used in the
electrolysis process, while the electric current is directly proportional to the electrical potential used [12]. When compared to the coating thickness of the anodized specimens using CA solvents, the about same thickness of the coatings was obtained for anodization using a TSA solution at a potential of 15 V.

According to AIPS 02-01-003 [10], the thickness of the standard anodizing layer should be within the range of 2-7 µm, while for the weight of the anodizing layer must meet the minimum weight of 22 mg/dm². The data in Table 2 shows that the treated specimen with TSA solution at 11 V did not meet the applicable standards because the thickness of anodized layer obtained was only about 1.51 µm. Meanwhile, the anodized layer thickness for other process has fulfilled the required thickness requirement. The data in Table 2 shows that the weight of the anodizing layer for all treatments weighed more than 22 mg/dm².

### Table 2 Coating weight and thickness measurement results

| Solution | Potential (V) | Coating Weight (mg/dm²) | Coating Thickness (µm) | 1  | 2  | 3  | 4  | 5  | avg. |
|----------|---------------|-------------------------|------------------------|----|----|----|----|----|------|
| TSA      | 11            | 53.56                   | 1.53                   | 1.36| 1.53| 1.45| 1.7 | 1.514|
|          | 13            | 66.71                   | 2.22                   | 2.73| 2.39| 2.3  | 2.22 | 2.372|
|          | 15            | 90.76                   | 3.07                   | 3.24| 3.07| 2.56| 2.82 | 2.952|
|          | 17            | 102.32                  | 3.58                   | 3.5 | 3.58| 3.5  | 3.33 | 3.498|
|          | 19            | 124.74                  | 4.35                   | 4.1 | 4.61| 4.27| 4.61 | 4.388|
|          | 21            | 130.13                  | 4.7                    | 4.87| 5.21| 4.52| 4.52 | 4.764|
| CA       |               | 54.66                   | 3.07                   | 2.9 | 2.9 | 2.82| 3.07 | 2.952|

3.2. **Corrosion resistance test with Salt Spray Test (SST)**

The corrosion resistance test using a salt spray test method (SST) was performed in a salt spray chamber by spraying a 5% NaCl solution onto the specimen surface. The tests were performed for all specimens, both anodized, sealed, and unanodized specimens. Surface observations carried out on specimens that have been salt spray tested. The corrosion hole formed on the surface of the post-salt spray specimens was observed and calculated.

Table 3 shows the compilation of a number of holes and the changes that occur on the surface of the specimens after being sprayed by salt. In Table 3 it was shown that unanodized specimens and specimens with TSA-11 V treatments experienced severe corrosion on the surface, while specimens for other treatments, did not undergo any changes or corrosion on the surface.

According to ISO 9227, the maximum number of hole densities formed on the surface of the sample after SST is 2 holes / dm² and there should be no hole having a diameter greater than 0.8 mm. With this result, it can be said that the specimens treated with solutions of CAA, TSA-13 V, TSA-15 V, TSA-17 V, TSA-19 V, and TSA-21 V have met the applicable standards.
Table 3 Result of specimen surface observation after salt spray test

| Solution | Potential (V) | Number of pits |
|----------|---------------|----------------|
|          |               | 1  | 2  | 3  |
| TSA      | 11            | SC | SC | SC |
|          | 13            | 0  | 0  | 0  |
|          | 15            | 0  | 0  | 0  |
|          | 17            | 0  | 0  | 0  |
|          | 19            | 0  | 0  | 0  |
|          | 21            | 0  | 0  | 0  |
| CAA      | 0             | 0  | 0  | 0  |
| Unanodized |          | SC | SC | SC |

*SC = surface corrosion

3.3. Potentiodynamic polarization curve

The salt spray test has not been able to determine what treatment produces the best corrosion resistance. Therefore, a potentiodynamic polarization measurement was performed. The corrosion potential and current density of corrosion is obtained by extrapolating the cathodic Tafel equation. The polarization curves of each specimen are shown in Figure 1. The results of the measurement of the corrosion density and the corrosion density are shown in Table 4.

*Fig 1 Potentiodynamic polarization curve*
In Figure 1 it is seen that the polarization curves of each sample do not appear to have a clear passive area. According to Moreto et al. [13], this suggests that pitting corrosion occurs naturally when it reaches corrosion potential, so in this case, the potential for corrosion can be said to be equal to its pitting potential. The corrosion density occurring in anodized specimens is much lower than that of unanodized specimens. Among all anodized specimens, the lowest corrosion current density occurs on a TSAA-15 V specimen. The small corrosion current density indicates that the flow of electrons flowing in the oxidation process on the metal surface is also low. The TSAA-15 V specimen also shows a smaller corrosion density value than the CAA specimen. That is, the corrosion resistance of TSAA-15 V specimens is better than CAA specimens.

Table 4 Corrosion potential and corrosion current density measurement

| Specimen   | $E_{\text{corr}} = E_{\text{pitt}}$ (V vs Ref.) | $I_{\text{corr}}$ (µA/cm²) |
|------------|---------------------------------------------|-----------------------------|
| unanodized | -0.713                                      | 3.415                       |
| TSAA 11 V  | -0.677                                      | 0.84                        |
| TSAA 13 V  | -0.668                                      | 0.231                       |
| TSAA 15 V  | -0.64                                       | 0.014                       |
| TSAA 17 V  | -0.682                                      | 0.909                       |
| TSAA 19 V  | -0.655                                      | 0.04                        |
| TSAA 21 V  | -0.675                                      | 0.479                       |
| CAA        | -0.699                                      | 0.305                       |

3.4. SEM-EDS analysis results

SEM is used to observe the coatings formed on the cross section of anodized specimens. The specimens observed were CAA and TSAA-15 V specimens. The TSAA-15 V specimens were selected because from the previous test, the specimens had the best corrosion resistance and coating thickness close to CAA specimens. The anodizing layer is also tested for analyzing the chemical composition. Figure 2 shows the cross-sectional observations of the two specimens. From Figure 2 it can be seen that anodized specimens with TSAA-15 V and CAA treatments produce a layer of oxide on its surface, with a similar thickness. In Figure 3 it is shown that the chemical composition of the coatings formed on the surface of the specimens is dominated by oxygen and aluminum atoms.

Fig 2 Cross section of the a) CAA specimen and b) TSAA-15 V specimen
In the anodizing layer of TSAA-15 V specimen contains about 29.13% aluminum atoms and 70.87% oxygen atoms, whereas in the anodizing layer of CAA specimen contain 34.60% aluminum atoms and 65.40% oxygen atoms. The ratio of Al:O in anodized layer on TSAA specimen is 2:4.67, while on CAA specimen is 2:3.71. Theoretically, the Al:O ratio for the anodizing layer is 2:3 because the phase formed is Al₂O₃. However, in both specimens there are excess oxygen atoms. According to Arenas [8], it can be due to the presence of residual acids trapped in the sealing later, so the anodizing layer becomes richer in oxygen.

**Fig 3** EDS chemical composition analysis for a) TSAA-15 V specimen and b) CAA specimen

Specimens that have been tested for salt spray (SST) were observed under SEM to compare their surface before and after the test. Surface specimens observed were for specimens with TSAA-15V and CAA treatments, as well as unanodized specimens. The surface appearance of the specimens is shown in Figure 4.

In Figure 4, the unanodized specimen appears to have severe surface corrosion after SST. Before SST, the specimen appears to have several holes that are the location of pitting corrosion. Unanodized specimens will be susceptible to corrosion attack, either surface corrosion or pitting corrosion. Meanwhile, for TSAA-15V specimens, it was shown that prior to SST, the specimen surface tended to be smoother (had fewer holes) than the unanodized specimens. After SST, there appeared to be some large, elongated bumps, but did not appear to damage the surface of the specimen compared to unanodized specimens. The bump may be the initiation of filiform corrosion [14]. The same lump was also observed on CAA specimens.
4. Conclusion
In the anodizing process of aluminum 7075 T6 using TSA solution, the greater the anodizing potential the thicker and heavier the anodizing layer. In the 7075 T6 aluminum alloy, the TSAA-15 V treatment provides the best corrosion resistance compared to TSAA treatments using potentials of 13, 17, 19, and 21 V. For the same coating thickness, the corrosion resistance of the TSAA-15 V specimens is better than the specimens treated by CAA.
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