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#### EFFECT OF SULFURIC-TARTARIC MIXED ACID ANODIZATION ON THE CORROSION BEHAVIOUR OF HEAT-TREATMENT ALUMINIUM ALLOY 6061 IN NaCl

M. Salisu<sup>1,2</sup>, A. G. Isah<sup>2</sup> and M. U. Garba<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Federal University of Technology, Minna, Niger State, Nigeria.

<sup>2</sup>Scientific Equipment Development Institute, Minna, Niger State, Nigeria.

**Abstract:** Effect of sulfuric-tartaric acid anodization on the corrosion behaviour of as-cast, heat treated and heat treated plus anodized aluminium alloy (AA 6061) in 0.5 M sodium chloride (NaCl) was investigated using weight loss. To compare the effectiveness of the anodization, both anodized and unanodized coupon samples were subjected to the corrosion test. The corrosion rate was determined in 0.5 M NaCl medium. Weight losses of coupons were taken at interval of 72 hrs (3 days) over a period of 504 hrs (21 days). The result obtained shows an initial increase in corrosion rate for both anodized and unanodized coupons then followed by a decrease which is tenable in normal corrosion rate profile. In comparison the unanodized coupon samples corrode faster than the anodized. It was concluded that anodization inhibit the corrosion rate of aluminium alloy 6061 in NaCl medium.

## 1. INTRODUCTION

Aluminium alloy (AA 6061) is one of Al-Mg-Si (6xxx series) alloys were reported to have good corrosion resistances and optimum strength when subjected to solution heat treatment followed by quenching and tempering treatment (age-hardening) (Maisonnette *et al.*, 2011). The alloy is characterized to have better formability, weldability and lower density when compared with other aluminium alloys, hence resulted to their wide applications in the transport and the public domains (framework, pylon, handling equipment to mention but a few) and also for complex structures assembled by welding (Maisonnette *et al.*, 2011). Improving the strength of 6xxx series aluminium alloys by age-hardening is associated with the formation of magnesium silicate (Mg<sub>2</sub>Si) precipitates. The presence of precipitates however, which are advantage to microstructural heterogeneity for strength development equally are setback to electrochemical heterogeneity for corrosion resistance (Kairy *et al.*, 2016). Thus, an increase in the alloy strength from precipitates is associated with increased susceptibility to localized corrosion such as pitting and intergranular corrosion (IGC) (Liang *et al.*, 2013).

The need to tackled the localized corrosion that do emanate amid heat treatment become necessary because the effect of unchecked corrosion therefore does not end up with the corroding utility itself but also covers the wide range of man and his economic and social welfare. The most commonly used corrosion control methods are materials selection and design, using corrosion-resistant alloys, protective coatings; use of special heat treatment; corrosion inhibitors. All of these methods are appropriate for controlling corrosion in certain situations and not for others. They are often used together to solve a particular corrosion problem (Madakson *et al.*, 2012). However, in order to improve their superficial mechanical properties, anodizing has been mostly used (Bensalah *et al.*, 2012).

Anodizing of aluminium is a well-known electrochemical surface treatment during which an anodic oxide layer is formed on an aluminium anode. Different electrolytes are

commonly used, leading to the formation of a porous oxide with pore diameters and barrier layers membranes up to 200  $\mu\text{m}$  thick. The electrolytes that can be used include chromic acid, sulphuric acid, oxalic acid, phosphoric acid, borates, citrate and carbonates while employing either alternating or

direct current (Sheasby, 2001; AlaaV *et al.*, 2013). Hydrothermal treatment which is also known as sealing is carried out in order to render the coating impermeable and non-absorptive to chemicals and other solutions (Sheasby, 2001; SaeedikhaniV *et al.*, 2013).

Chromic acid electrolyte is an effective way to produce oxide films with excellent resistant to corrosion during anodization. However, due toxicity of chromium it has since been prohibited. In order to find alternative to chromic acid electrolyte, several studies have been investigated using different acid electrolyte acids (Bensalah *et al.*, 2012; Saeedikhani *et al.*, 2013; Mubarak *et al.*, 2015). Example of these acid electrolyte include boric-sulphuric acid (Thompson *et al.*, 1999), sulphuric acid (Madakson *et al.*, 2012), sulphuric-boric-phosphoric acids (Saeedikhani *et al.*, 2012), sulphuric acid, oxalic acid, phosphoric acid (Abd-Elnaiem *et al.*, 2013), phosphoric acid, sulphuric acid (Liu *et al.*, 2014), sulphuric acid (Canepa *et al.*, 2016) and sulphuric acid (Dumitrascu and Benea, 2017). Recently, the mixture of tartaric-sulphuric acid shows more promising results as an inhibitor and reduces dissolution of anodic oxide film and better corrosion protection performance. A number of works have been reported on the application of tartaric-sulphuric acid for anodization; Boisier *et al.* (2008) investigated the effect of tartaric acid on anodic film morphology and on corrosion resistance of hydrothermally sealed anodized AA 2024, It was observed that the properties of the barrier layer were higher when sealing was performed on specimens anodized in the presence of tartaric acid. This suggests a specific role of the species on the barrier layer, which contributes to the enhancement of the performance in terms of corrosion resistance of the sealed anodic films. On related report Mubarak *et al.* (2015) reported the influences of anodizing parameters of Al 2024 T3 in tartaric-sulphuric acid on the



thickness, weight and corrosion resistance of the anodize layer. The authors demonstrated that the most influencing factor that determines the thickness and weight of the anodize layer is temperature, voltage and duration. The findings of the research reveal that pit density and current density were dependent on the coating thickness. Similarly, Fu *et al.* (2015) reported the effect of tartaric-sulphuric acid concentration on the anodic behaviour of titanium alloy, it was observed that 30 g/L tartaric acid addition to sulphuric acid increased the thickness of anodic film, decreased the crystallinity and weakened the dissolution rate of anodic film.

Based on the literatures reviewed so far sulfuric-tartaric acids electrolyte provided friendly environmental process and improved corrosion resistance; however the use of sulfuric/tartaric acid on the anodization of aluminium alloys (AA 6061) was poorly reported. This study proposed the use of electrolyte containing sulfuric-tartaric acids for the anodizing of 6061 aluminum alloy.

## 2. MATERIALS AND METHOD

The materials and equipment used during the experiments include 6061 Aluminum alloy. Quenching medium, melting furnace, heat treatment furnace, grinding machine, rotary wheel polishing machine, etching reagent, sulphuric-tartaric acid, hydrochloric acid, digital weighing machine, electrifier, and auxiliary wares for anodization set up.

### 2.1 Aluminium Alloy 6061 Development

For this study, the aluminium alloy (AA 6061) was prepared from aluminium cable wire (cut into smaller pieces) and weighed to 5 kg, magnesium metal powder and silicon carbide. Melting was conducted using charcoal-fire crucible. The molten metal was then poured into a cylindrical sand mould (350 mm length by 20 mm diameter) and allowed to cool. The cast alloy was then ejected from the mould and machined to sample size of 14 mm diameter and 10 mm length.

In order to determine the actual chemical composition of the cast AA 6061, an X-Ray Fluorescence (XRF) analysis was carried out on the cast specimen. The analytical result is shown in Table 1.

### 2.2 Anodization Process

Before the anodizing operation the surface of the samples were pre-treated with solution of 0.5 M NaOH for 5 min at 45°C and desmutting in 5 vol.% HNO<sub>3</sub> for 5 min at 25°C (Talib and Khalid, 2015); anodization operation was carried out in a mixed electrolyte of sulfuric-tartaric acid (40 g/l H<sub>2</sub>SO<sub>4</sub> + 80 g/l C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>) at a voltage of 12-13 V, period of 20 min and temperature 37°C (Capelossi *et al.*, 2015). After each steps, the specimens were neutralized by rinsing in distilled water to avoid contamination of solution of the subsequent operations. The details for the procedure can be found in (Sadikhani *et al.*, 2013).

### 2.3 Weight Loss Corrosion Coupon Analysis

All test coupons were cleaned, weighed and stored in a dessicator. The weighed coupons completely immersed in 250 ml bowl containing the corrosive media (0.5 M NaCl). Weight losses of coupons were taken at interval of 72 hrs (3 days) over a period of 504 hrs (21 days). Prior to weight measurement of each coupon, the surface was scrubbed with

brush in distilled water and then rinse in ethanol in order to remove corrosion product and then air dried. The weight loss was calculated by taken the differences between the weight before immersion and the weight after immersion. Each weight was measured to the nearest 0.01 g on a laboratory weighing balance.

Calculation of the corrosion rate will be in mm/year, by applying the formula;

$$CPR = \frac{87.6 \Delta W}{DAT} \left( \frac{mm}{yr} \right) \quad (1)$$

Where;

$\Delta W$  = weight loss in mg =  $W_o - W_f$ ,  $W_o$  = original weight of the coupons,  $W_f$  = final weight of the coupons after 3 days,  $D$  = density of aluminium alloy in g/cm<sup>3</sup> = mass/volume of substance,  $A$  = total surface area of the samples in cm<sup>2</sup>,  $T$  = exposure time in hours, in the corrosive medium (Madakson *et al.*, 2012).

## 3. RESULTS AND DISCUSSION

The results obtained after successfully conducting the experiments are as follows:

### 3.1 Chemical Composition Analysis of the Cast AA 6061

The result of the X-ray fluorescence (XRF) analysis was carried out using EDXRF Model: Minpal 4 No. DY 1055 manufactured by PANalytical B.V and the result is presented in Table 1.

TABLE 1: CHEMICAL COMPOSITION (wt. %) OF CAST AA 6061

Element	% Composition				
	This work	1	2	3	ASTM
Al	95.93	Bal	Bal	89.68	95.80 – 98.61
Si	0.7	0.15	0.4	4.42	0.4 – 0.8
Fe	0.5	0.4-0.8	0.2	0.63	0.0 – 0.7
Cu	0.35	0.15-0.4	0.15	0.14	0.15 – 0.4
Mn	0.15	0.7	0.15	2.06	0.0 – 0.15
Mg	1.1	0.8-1.2	0.8	2.52	0.8 – 1.2
Cr	0.9	-	-	0.02	0.04 – 0.35
Zn	0.25	0.25	0.25	0.65	0.0 – 0.25
Ti	0.12	0.15	-	0.01	0.0 – 0.15

Source: 1 Dumitracus and Benea, 2017, 2 Abubakre *et al.*, 2009, 3 Yu *et al.*, 2002

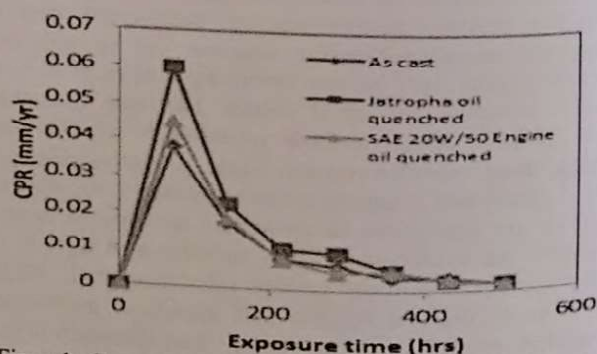


Figure 1: Corrosion Rate of Unanodized Al alloy 6061 As-cast, Jatropha oil quenched, and SAE 20W/50 Engine oil quenched samples Against Exposure Time in 0.5 M NaCl solution



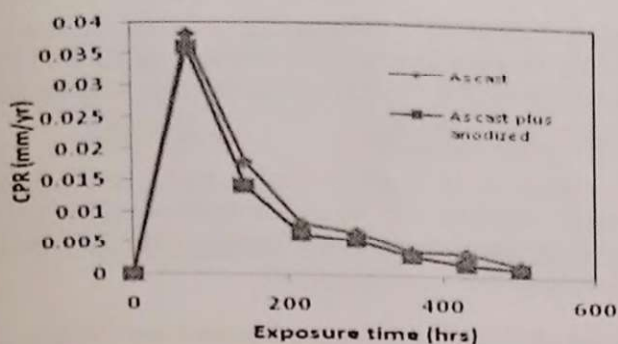


Figure2: Corrosion Rate of Unanodized and Anodized Al alloy 6061 As-cast samples Against Exposure Time in 0.5 M NaCl solution

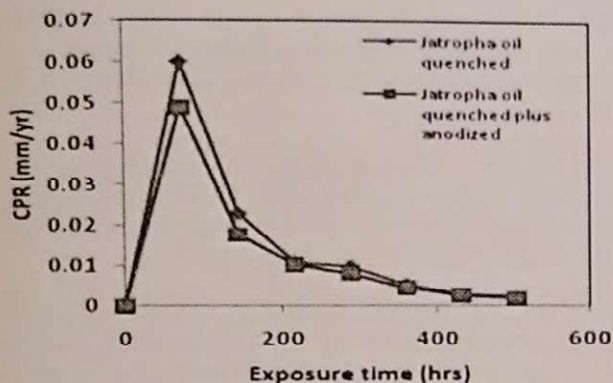


Figure3: Corrosion Rate of Unanodized and Anodized Al alloy 6061 As-cast, Jatropha oil quenched samples Against Exposure Time in 0.5 M NaCl solution

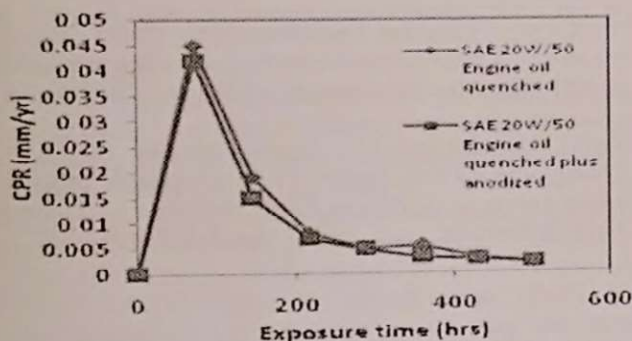


Figure4: Corrosion Rate of Unanodized and Anodized Al alloy 6061 SAE 20W/50 Engine oil quenched samples Against Exposure Time in 0.5 M NaCl solution

### 3.1.1 Chemical Composition Analysis of the Cast AA 6061

Aluminium alloy (AA 6061) is one of Al-Mg-Si (6000 series) (Kairy *et al.*, 2015). The composition (in wt.%) obtained for this research was 95.93Al-1.1Mg-0.7Si. This value falls within the range of Yu *et al.*, (2002) who reported 96.20 Al- 0.8-1.2 Mg-0.15Si and also with the value of ASTM B247 as 95.7999-98.6099 Al- 0.8-1.2 Mg-0.4-0.8Si but with slight difference with Dumitracus and Benea (2017) who reported 97.86 Al-0.8 Mg-0.4Si. However, with contrast with Abubakre *et al.* (2009) who reported 89.6875Al- 2.1515 Mg-4.4174Si. The inconsistency in the result could be attributed to the raw material and operating condition of casting.

### 3.1.1 Effect of Heat Treatment and Anodization on the Corrosion Resistance of AA 6061

The results of corrosion penetration rate (CPR) of unanodized and anodized AA 6061 coupons exposed to sodium chloride (0.5 M NaCl) solution at interval 72 hrs (3 days) over a period of 504 hrs (21 days) are shown in Figure 2-4. The corrosion penetration as a function of time is shown in Figure 1-4, from Figure 1 shows the corrosion rate attained the highest point of 0.060 mm/yr for sample quenched in Jatropha oil before it begin to declined, follow by sample quenched in SAE 20W/50 which attained the highest point of 0.038 mm/yr then finally as cast recorded the least point of 0.038 mm/yr before decline. This variation may be attributed to the quenching effect in a different media.

From Figure 2-4. Generally we experienced initial increase in corrosion rate for both anodized and unanodized coupons then followed a decrease with exposure time. This result demonstrated the normal corrosion rate profile of passivating metals when subjected to corrosive environments. Aluminium is known to belong to this group. The nature firstly rise in the corrosion rate going with the active region until it attained the highest point leading to formation of oxide on the samples metal the corrosion rate decreases due to passivity. At certain stage there was fluctuation of increase then decrease this could be as result of trans-passivity region. In comparison the unanodized coupon samples corrode faster than the anodized.

### CONCLUSION

The effect of sulphuric-tartaric acid anodization on the corrosion behaviour of heat treated AA 6061 has been studied in sodium chloride. As result of this investigation, it was revealed that both as-cast and heat treatment aluminium alloy 6061 corroded in sodium chloride solution with heat treated sample been the fastest. Anodization with sulphuric-tartaric acid electrolyte reduced the corrosion rate of aluminium alloy 6061 in sodium chloride solution. It was concluded that sulphuric-tartaric acid can be used as electrolyte to improve the corrosion resistance of aluminium alloy 6061.

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