THE MORPHOLOGY AND ELECTROCHEMICAL STUDIES OF AC ANODIZED SS304L UNDER VARIOUS ANODIZING CONDITIONS

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Abstract. A novel method of anodizing stainless steel (SS) 304L with alternating current (AC) as the power source is presented in the interest of producing a porous oxide film. Since there is a scarcity of research on AC anodizing, this research work is focused on the electrochemistry and morphology of the oxide film generated on the SS304L. The anodizing is done in an ethylene glycol solution containing different concentrations of ammonium fluoride, NH_4F, varying from 0.5 wt.% to 7 wt.%. The anodizing voltage is fixed to 40 V and the process is carried out at 25 ºC for 30 minutes. The electrochemical studies using the Tafel polarization method in terms of corrosion rate showed decreased values from 0.2842 mm/year to 0.1026 mm/year of the as-received, and anodized 3.0 wt.% specimens, respectively. For morphological studies, the oxide film formed on the anodized SS304L is characterized using a scanning electron microscopy (SEM) and the thickness of the oxide film formed is recorded using 3D profilometer. The morphology demonstrated the formation of the porous arrangement with localized parts of the surface oxide layer and the thickness of the oxide film rises at 2.65 µm and 4.29 µm, respectively, when the NH_4F concentration increases from 0.5 wt.% to 1.0 wt.%. This indicates that there are significant advantages of using AC anodizing on stainless steel.

Keywords: Stainless steel 304L, anodizing, oxide film, corrosion

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Introduction

Nanomaterials have recently gained a lot of interest due to their remarkable properties at the nanoscale. The nano-porous structure that formed on the surfaces of the materials aided in a variety of applications, including solar hydrogen and fuel cells, batteries, sensors, power generation, and batteries [1]. The majority of research on these anodized nano porous structures has concentrated on alloys such as aluminum, titanium, magnesium, and, most recently, stainless steel [2]. The major ingredients of stainless steel are iron or ferrous alloys in combination with other components. The three primary forms of stainless steel that are known for their high quality are austenitic stainless steel, ferritic stainless steel, and martensitic stainless steel. Type 304L, austenitic stainless steel, is the most often utilized in our environment, where the L stands for extra-low carbon percentage [3].

Anodizing is a technique for forming an anodic oxide coating or nano porous structure on the surface of alloys. Although anodizing metals such as Al, Mg, and Ti is a well-established method, stainless steel is gaining popularity [4]. Grimes et al. conducted the first work on iron anodization using an iron substrate and an ethylene glycol solution containing H_2O and NH_4F [5]. A variety of factors can influence the nano porous oxide film that is produced. The parameters include the anodizing process's type, concentration, temperature, and length, as well as the current or voltage utilized [6]. The standard anodizing process involves two stages, wherein the initial phase involves chemical etching of the stainless steel. However, the etching technique used in this process results in liquid pollution due to chemical corrosion [7].

The anodizing process could be powered by either direct current (DC) or alternating current (AC). Extensive research has been conducted on the use of direct current (DC) as a power source for stainless steel. AC anodizing is often used on Al, Mg, and Ti alloys and is preferred over DC anodizing because it can prevent the build-up of gas bubbles, resulting in a more uniform and dense oxide layer with better corrosion resistance. However, only a few studies on the AC anodizing of stainless steel were carried out. The purpose of this study is to analyze the formation of porous oxide film on SS304L by AC anodizing in terms of surface morphology and electrochemical characterization at room temperature.

Materials and Methods

Material and Chemical Preparation

The raw material was stainless steel 304L (SS304L) plate, which was cut into a rectangle shape sized 25 mm by 15 mm by 2 mm. After being ground to 1200 grit paper, the specimens were polished with diamond paste to a mirror-like surface. After an acetone degreasing, the specimens were rinsed with distilled water. Electroplating tape was implemented on the specimens to ensure that only one surface was exposed throughout the anodizing procedure. The electrolyte was a solution of 3 wt.% water in ethylene glycol and ammonium fluoride ranging from 0.5 wt.% to 7 wt.%. The specimens were austenitized and quenched for one hour at a heating rate of 2 °C per minute and a temperature of 700 °C.

AC Anodizing of SS304L

The anodizing experiment was designed with a basic anodizing setup, equipped with an AC power source, and the electrodes selected for both cathode and anode, were SS304L. The anodizing process took 30 minutes at room temperature with a 40 V anodizing voltage. Following the anodizing process, the anodized SS304L was thoroughly rinsed with distilled water and dried using an air blower for further analysis.

Morphology and Electrochemical Characterization

A profilometer is a device that measures the surface profile of a desired object to detect its surface roughness, texture, waviness, surface step height, and deposited oxide film thickness. It is used to analyze anodized specimen thickness, depth, and surface roughness. Profilometers are classified into two types: stylus profilometers and optical profilometers. In this study, an optical profilometer was employed, which utilizes light as its probing mechanism. The working principle of the optical profilometer involves directing light onto the surface of the sample to detect it in three dimensions, resulting in a 3D representation.

Scanning electron microscopy (SEM) is a microscopy technique that enables the capture of high-resolution images of samples using electrons. SEM using a high-energy electron beam would further react with the atoms and generate several signals that transmit information to the sample. It starts with the generation of second or backscattered electron beams from a tungsten filament cathode electric gun. As a result, topographic, morphological, and compositional information can be noticed. The SEM model JEOL JSM-6460-L was used to analyze the surface morphology of the porous oxide film of anodized SS304L.

NOVA software and AUTOLAB PGSTAT 204 were both implemented for the linear polarization test. The test was carried out in 3.5% sodium chloride, NaCl, using a three-electrode corrosion cell method. The specimen with an exposed area of 1 cm^2 acted as the working electrode, while the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum rod. To assure that the exposed area of the specimens was 1 cm^2, electroplating tape was used. To reach a steady state, the open circuit potential (OCP) is determined for 30 minutes. When no potential or current is provided to the corrosion system, the OCP is the potential of the working electrode relative to the reference electrode. The significance of this is that it enabled the determination of how the specimens would interact with the electrochemical corrosion reactions of the medium. The polarization scanning rate was 10 mVs^{-1}, and the scan potential range was -0.8 V to 1.0 V versus SCE.

Results and Discussion

Electrochemical Characterization

The results of the Tafel polarization test of the specimens in 3.5% NaCl are summarized in Table 1. Figure 1 shows that the Tafel polarization curve of as-received specimen and anodized specimens of different NH_4F concentrations. Extrapolating the polarization curve in Figure 1 yields the corrosion potential (E_{corr}) and corrosion current density (i_{corr}). E_{corr} evaluated the likelihood of corrosion during the test, while i_{corr} calculated the severity of the corrosion. The E_{corr} value of the as-received specimen, which had no film formed on the surface, was -0.3231 V. The E_{corr} values of anodized specimens of 3 wt.% and

5 wt.% have been changed to more positive values, -0.3087 V and -0.3153 V, respectively. The lower the corrosion rate of the specimens, the higher the E_{corr} value. As for 0.5 wt.%, 1.0 wt.% and 7 wt.% showed more negative value of E_{corr} compared to the as-received specimens which were -0.3231 V, -0.3300 V and -0.6291 V, respectively. The corrosion rate also indicated a higher rate. This is due to the porous oxide film formed [8].

Table 1: Result of polarization test for as-received and different concentration range of NH_4F specimens

Specimens	E_{corr} (V)	i_{corr} (A/cm^2)	Corrosion Rate (mm/year)
As-received	-0.3231	3.471×10^{-6}	0.2842
0.5 wt.%	-0.3837	3.451×10^{-6}	0.3044
1.0 wt.%	-0.3300	4.834×10^{-5}	0.4582
3.0 wt.%	-0.3087	3.721×10^{-6}	0.1026
5.0 wt.%	-0.3153	2.619×10^{-6}	0.1154
7.0 wt.%	-0.6291	6.644×10^{-4}	7.7198

It was clearly shown that the E_{corr} values for both 3.0 wt.% and 5.0 wt.% specimens were shifted to a more positive E_{corr} value compared to the as-received specimens as indicated in Figure 1. Both the 3.0 wt.% and 5.0 wt.% specimens exhibited enhanced corrosion resistance, attributed to the formation of a porous oxide layer on their surfaces [9]. The polarization curve of the AC specimen revealed the presence of a pitting potential, E_{pit}, which denotes the potential at which breakdown of the passive layer occurs.

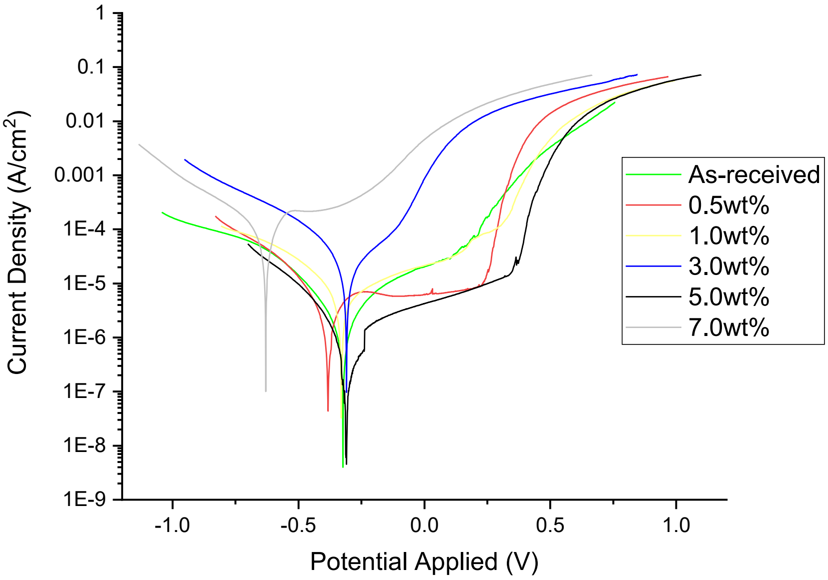

Figure 1: The Tafel polarization curve of as-received and anodized specimens using AC power sources in ethylene glycol solution with different concentration of NH_4F.

Surface Morphology of Anodized SS304L

Figure 2 shows the surface morphology of porous anodized SS304L specimens using a scanning electron microscopy (SEM) as the concentration of NH_4F increased from 0.5 wt.% to 7.0 wt.%. At low NH_4F concentrations of 0.5 wt.% to 3.0 wt.%, the generation of the porous arrangement with localised parts of the surface oxide layer occurs as shown in Figure

2(a) to (d). At 0.5 wt.%, the oxide film formed was cragged and when the percentage of NH_4F was increased to 1.0 wt.%, the oxide film was more even. The oxide film formed was more compact as the concentration increased to 3.0 wt.% and 5.0 wt.%. As for 7.0 wt.% specimen, the oxide film formed was more disarranged. This can be regarded as insufficient chemical dissolution of oxide. In contrast, when the fluoride ion level increases, the chemical dissolution of oxide accelerates, culminating in the disintegration of the porous layer.[10].

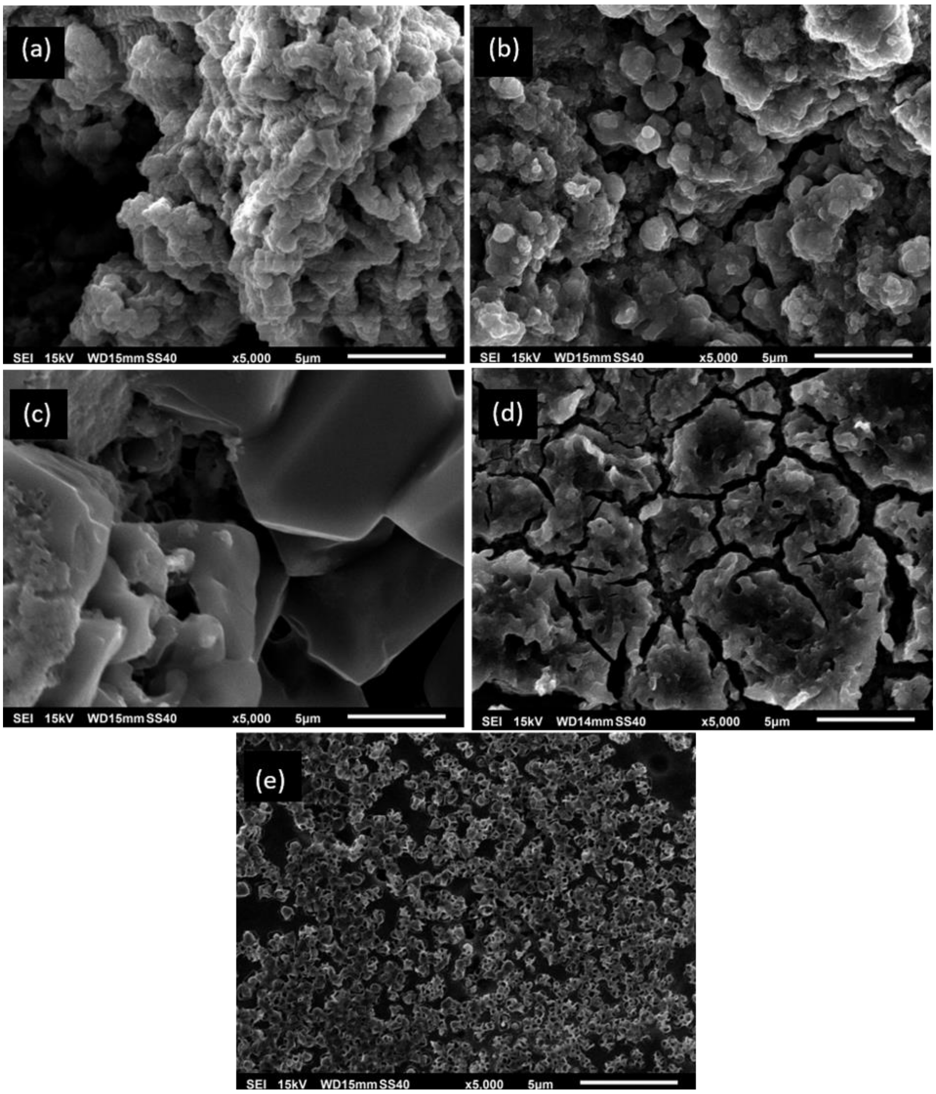

Figure 2: SEM micrographs of anodized specimens with different NH_4F concentration (a) 0.5 wt.%, (b) 1.0 wt.% (c) 3.0 wt.%, (d) 5.0 wt.% and (e) 7.0 wt.%

Thickness and Depth of Anodized SS304L

Table 2 shows the thickness and depth of the porous oxide layer formed on the anodized SS304L in ethylene glycol solution with different NH_4F concentration. The data were separated into the thickness of the oxide film and the depth found on the surface of the specimens, as shown in Figure 3. The thickness of the generated oxide films was only detected on the 0.5 and 1.0 wt.% specimens. The thickness of the oxide layer generated increases as the concentration of NH_4F increases, but only at 0.5 wt.% and 1.0 wt.% specimens, where the thickness reported was 2.65 μm and 4.29 μm, respectively. However, the anodizing process caused the specimens to erode or dissolve, causing the thickness of the specimens to be reduced, as shown in Figure 3. The depth decreases as the concentration of NH_4F increases.

Table 2: Thickness and depth of anodized specimens obtained using a 3D profilometer

Concentration of NH_4F (wt.%)	Thickness Oxide Layer (µm)	Depth (nm)
0.5	2.65	7.14
1.0	4.29	6.33
3.0	-	6.00
5.0	-	4.59
7.0	-	2.94

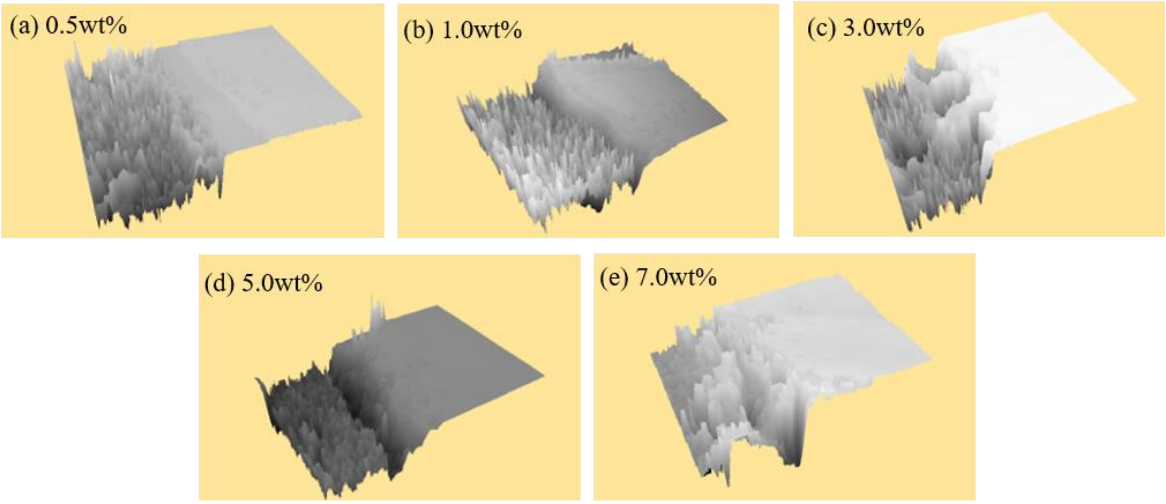

Figure 3: The 3D image from an optical profilometer depicted the morphologies of two phases of the specimens that were exposed and not exposed to the anodizing process with different NH_4F concentration (a) 0.5 wt.%, (b) 1.0 wt.% (c) 3.0 wt.%, (d) 5.0 wt.% and (e) 7.0 wt.%

Conclusions

Anodization of SS304L using AC power sources was performed in an ethylene glycol solution containing varying concentrations of NH4F ranging from 0.5 wt.% to 7.0 wt.% and 3% H_2O to produce oxide films. Electrochemical studies utilizing the Tafel polarization method indicated a reduction in the corrosion rate from 0.2842 mm/year to 0.1026 mm/year for as received, and anodized 3.0 wt.% specimens, respectively. The development of an oxide film increased as the NH4F concentration increased from 0.5 wt.% to 1.0 wt.%, with thicknesses of 2.65 µm and 4.29 µm, respectively. However, the anodizing process resulted in metal dissolution, leading to a reduction in specimen thickness from 7.14 nm to 2.94 nm for NH4F concentrations of 0.5 wt.% and 7.0 wt.%, respectively.

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Author Contributions

All authors contributed to the data analysis, drafting, and critical revision of the paper, and they all agree to accept responsibility for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

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