

## Experimental Study Of Anodizing Process For Stainless Steel Type 304

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### Abstract

Stainless steels type 304 has widespread applications with excellent corrosion resistance to atmospheric environments. Therefore, a number of surface treatment technologies have been developed to further improve the localized corrosion resistance such as anodizing treatments. Anodizing process requires preparation of the surface, one of the most important finishing processes is electropolishing. This paper introduces a new experimental study of anodizing process for steel type 304. The effect of different variables (positive current density of 0.1-0.2 A/cm<sup>2</sup>, negative current density 0.011-0.066 A/cm<sup>2</sup>, nitric acid concentration 6 - 35 Vol. %, Sulfuric acid concentration 4-20 Vol. %, and time of exposure 5-15 mins. and temperature of electrolyte 5 - 50 °C.) were investigated. Finally, the experimental result found that the best conditions of anodizing are (positive cycle (0.1 A/cm<sup>2</sup>), negative cycle (0.03 A/cm<sup>2</sup>), 17% by vol. nitric acid and 8% by vol. sulfuric acid, temperature of (10°C), and time of (10 mins.).

**Keywords:** Anodizing, Steel type304,

### 1. Introduction

Photovoltaic panels (PV) have negative temperature coefficient which rising in panel temperature will decrease open circuit voltage by certain of V/°C. Solar chimney is passive elements and one of the most promising a natural power generator using the stack effect to induce buoyancy-driven airflow [1] which applied in different fields such as ventilation, drying process, or production of electricity systems. In addition, solar chimney utilizes solar radiation to increase the air temperature inside the SC channel and work as passive cooling PV panel through air flow in the channel.

Anodizing and electropolishing can substantially improve the corrosion resistance of stainless steels. The latter also provides a bright and shiny finish. Electrolytic treatment of stainless steels in acid electrolytes produces relatively thick oxide films and removes the adverse impurities in the oxide film [1, 2, and 3].

Frari et. al. (2009) [3] indicated that the nanoscaled morphology of the over layer covering stainless steels after electropolishing in perchloric acid-based electrolyte was explored mainly by AFM and SEM. Two kinds of stainless steels were tested. For the austenitic one (AISI 304L), a quasi-periodic arrangement of pores in this over layer was observed. Depending on the experimental conditions, the distance between neighbouring pores ranged from 20 nm up to 230 nm. This inter-pore distance varied either with the applied voltage or with the current density for a constant voltage. From XPS spectra performed on the nanostructured surfaces, analysis of the energy shifts of Cr and Fe 2p levels showed that the anodic overlayer was enriched in Cr atoms compared to the 304L steel bulk composition.

Mantel (2008) [4] indicated that anodizing treatments have been studied to improve adhesion of such modified surface in regard with epoxy adhesives. With H<sub>2</sub>SO<sub>4</sub> 5M-1200 mv and HNO<sub>3</sub> 50%-1200 mv treatments, metal dissolution is important. In opposite H<sub>2</sub>SO<sub>4</sub> 0.5M-980 mv and HNO<sub>3</sub> 50%-1050 mv

treatments exhibit a low metal dissolution, but polarization curves indicate the formation of secondary passive film. The other treatments are intermediate between dissolution and film formation. The average roughness is quite similar between the two first categories and the average value for Ra is around  $0.07\mu\text{m}$ . Treatments made at a high potential exhibit a higher roughness of around  $1.6\mu\text{m}$ . Chemical analyses of the anodized surfaces have been made using XPS and AES. The main results show that an increase in the film thickness is very well correlated with a chromium enrichment of the film. Chromium enrichment is often observed in films formed in acidic conditions and this is possibly due to the higher diffusivity and dissolution of iron cations.

Junqueira et. al.(2008) [5] studied the characterization of thin films using several high resolution techniques, such as FESEM, AFM, and depth-sensing indentation were performed on interference films grown on an AISI 304 stainless steel. The main results indicated that the coloration of stainless steel by a pulse current method results in the growth of a porous thin film on the steel surface, which in turn increases its surface roughness. These interference films mainly consist of hydrated chromium oxide containing iron. Increasing film thickness produces different colors and affects the mechanical properties of the coating-substrate system. Consequently, thicker films from (70-440) nm, such as those producing the gold and green colors, have proved to be softer but more abrasion resistant.

Fujimoto et.al.(2001) [1] investigated the extraordinarily thick and porous oxide films on type 304 stainless steel. The material was polarized in  $5\text{ kmol m}^{-3}\text{ H}_2\text{SO}_4$  solution at  $50\text{--}80\text{ }^\circ\text{C}$  with applied potential modulated as square wave. The films formed are classified into two types according to applied potentials. For the anodic type, Fe and Cr actively dissolve at the lower potential of the square wave, EL, into  $\text{Fe}^{2+}$  and  $\text{Cr}^{2+}$ , and then re-oxidize at the higher potential, EH, to be mainly  $\text{Cr}^{3+}$  oxide. Alternatively, for the cathodic type, Fe and Cr dissolve at EH, which is in the transpassive region, then the dissolved  $\text{Cr}^{6+}$  ions are reduced into  $\text{Cr}^{3+}$  oxide at EL. Transmission electron microscopy shows that the porous film consists of nanocrystalline grains of around  $20\text{--}30\text{ nm}$  in diameter, and has many pathways linking each other to be penetrated by ions and water molecules easily. The porous layer is basically composed of  $\text{Cr}_2\text{FeO}_4$  spinel oxide with excess Cr. The chemical composition, particle size, and also lattice parameter could be controlled by changing EH, EL, and the width of the potential pulse, tH and tL. The porous oxide films formed by square wave potential pulse polarisation might be applied for various surface functional materials, i.e. a carrier of catalyst, oxide electrode, and biocompatible materials.

This paper investigate the formation of anodic oxide film on stainless steel type 304 by means of nitric acid and sulfuric acid mixture at room temperature anodizing process with constant current density; in terms of current density, electrolyte concentration, temperature of electrolyte, and time of anodizing in order to study the effect of these four variables on film thickness growth on stainless steel.

## 2. Material And Methods

### 2.1 Mechanism Of Stainless Steel Anodic Film

Anodizing of stainless steels is carried out in a nitric and sulfuric acid mixture at room temperature. A power supply with an asymmetric AC square waveform is used with voltage control. Voltage control is critical for anodizing stainless steels. This is because chromium has two valence states, +3 and +6. Trivalent chromium forms an oxide film ( $\text{Cr}_2\text{O}_3$ ) on the stainless steel surface. However, hexavalent chromium in the form of  $\text{CrO}_4^{-2}$  or  $\text{Cr}_2\text{O}_7^{-2}$  is very soluble in aqueous solutions. When an applied potential is higher than the potential producing hexavalent chromium, the oxide film on stainless steels will dissolve in the acid electrolyte. Therefore, anodic oxide films on stainless steels can only be produced in a certain range of potential or voltage [2, 4].

Anodizing process using the above power supply consists of two cycles; positive and negative cycles.

During the positive cycle, substrate material beneath the oxide film converts to oxide film and sulfides in the film are oxidized to a soluble species. During the negative cycle, trivalent iron is reduced to divalent iron and hydrogen gas is evolved. The negative cycle is specially designed to help remove ferrous oxide in the film since ferrous oxide is much more soluble than ferric oxide in aqueous solutions. Ferrous oxide and sulfides in the oxide film on stainless steel are determined to be major sources of localized corrosion [1, 2, and 3].

The thickness of the anodic film can reach around 1000 angstroms, about 50 times thicker than the native oxide film and oxide films produced by passivation and electropolishing. The anodic oxide films are mainly composed of 80% chromium oxide (>80%) and nickel oxide (<20%) [2].

2.2 Materials

A. Anode

The specimens used for this study were stainless steel type 304 (source: Spain made) cut into the dimensions of (4×1×0.1) cm and were used as specimens for electropolishing, anodizing and corrosion tests. These specimens were examined at different variables (current density, acid concentration, time and temperature). Analysis of these specimens was carried out using (spark technique) in AL- NASER Company. Table (1) shows the results of nominal and analytical stainless steel type 304.

Table 1. The nominal results [6] and analytical stainless steel type 304.

Stainless steel analysis type	Elements										
	C	Mn	P	S	Si	Cr	Ni	Mo	Co	Ni	Fe
Nominal Wt% ASTM [101]	0.08 Max	2 Max	0.045 Max	0.03 Max	1 Max	18-20	8-10.5	0.38	0.12	0.056	66.345 - 74
Analytical Wt %	0.05	1.72	0.045	0.03	0.75	19.1	8.23	0.24	0.08	0.01	Balance

B.Cathode

The cathode consisted of titanium with dimensions of (2×6×0.03) cm coated with platinum to get the platinized titanium electrode using local pulsed laser deposition system and this was carried out in the Department of Applied Science/ Laser Science Branch, which has built such a system locally as shown in Figure (1).



Figure 1. The Pulse Laser Deposition System (PLD).

### 3. Experimental Procedure

#### 3.1 Mechanical Pre-Treatment

Raw materials of stainless steel were received in the form of plate. The plate was cut into small specimens into dimensions previously mentioned. They had sharp edges and then were chamfered via grinding wheel.

Prior to electropolishing and anodizing processes, the specimens were prepared in the following processes:

The specimens were ground using Amery paper with grade of 600, 800, 1000 grit water-cooled silicon carbide papers. Care was taken, particularly when grinding austenitic grades, to remove the cold work from cutting and from each grinding step. In general, grinding times are 1 to 2 minutes per step. Grinding is carried out by hand; the specimen is rotated 45 to 90° between each step.

After grinding, specimens are usually rough; the specimens should be finally polished using fine abrasives. The most commonly used final abrasives are 1 micron diamond as a paste on red felt cloth, used extender to moisten the cloth and reduce drag. A wheel speed of approximately 250 rpm is used. Polishing times are 2 minutes per step. For hand polishing, rotate the specimen around the wheel in the direction opposite to wheel rotation while moving from center edge.

The stainless steel specimens were treated by using solutions of various concentrations of 10% by vol. HNO<sub>3</sub>, 30% by vol. HCL, 30% by vol. glycerin and 30% by vol. alcohol as etching solution for 30 sec to remove the black layer that was formed on the surface. Afterwards, the specimen was rinsed with tap water followed by distilled water [7].

The electropolishing bath used for polishing 304 stainless steel is at concentration of 48% by vol. Phosphoric acid, 32% by vol. sulfuric acid, 10% by vol. glycerol and 10% by vol. distilled water and using the variables of current densities, times, and temperatures for electropolishing specimens, it was found that the best brightness, smoothness and weight loss measurements are observed with applied current density of 0.55 A/cm<sup>2</sup> and temperature 95 °C for time of 10 mins.

#### 3.2 Anodizing Process

Anodizing of 304 stainless steels was carried out in 250 ml capacity beaker containing 200 ml of acid mixtures solution in water bath type (Thoms Scientific) with temperature control. The stainless steel specimen was immersed in the anodizing solution and connected to the positive terminal of a local made an asymmetric square waveform AC current density. The cathode used is platinized titanium which was connected to the negative terminal of the above power supply. Both positive and negative terminals were submerged in a solution of nitric and sulfuric acid mixture in a temperature controlled bath of electrolyte. A power supply with an asymmetric AC square waveform was used with voltage control as in Figure (2). These specimens were examined under different variables mentioned in Table (2) below (current density, acid concentration, time and temperature).

Compressed air was pumped at a constant rate; water bath temperature was adjusted to the required value. When all the requirements of experiment were set up, the power supply was switched on so that a constant current was obtained. The parts were immersed in the solution while the power supply was switched on.

Table 2. Anodizing conditions; current density, acid concentration, time and temperature [8].

Condition	Value ranges
Positive current density	0.9 - 1.8 Amp.
Negative current density	0.1 - 0.6 Amp.
Nitric acid concentration	6 - 35 Vol. %.
Sulfuric acid concentration	4 - 20 Vol. %.
Temperature of electrolyte	5 - 50 °C.
Time of exposure	5 - 15 min.

Anodizing method provides a protection for the specimens from dissolution, also care has been taken during the loading specimen in order to prevent short circuit i.e. burning the surface. Before the power supply is switched on, current density must be fixed at the desired value, when power supply is switched on the voltage increases gradually and the current density is maintained at the fixed value for the remaining time of the experiment. At the end of the desired time, the power supply is switched off and the anode is removed from anodizing cell immediately to prevent the dissolution of anodic film. The specimen is rinsed with running tap water followed by distilled water to remove the excess solution on it and then dried in air and weight loss measurements for the specimen are obtained using Electronic balance.



Figure 2. The anodizing cell.

### 3.3 Anodizing of 304 Stainless Steel

The anodizing process was carried out using beaker of (250 ml) which contained of mixture solution of 17% by vol. nitric acid and 8% by vol. sulfuric acid placed in an electrolyte controlled bath temperature at 10 oC.

A power supply with an asymmetric AC square waveform was used with voltage control. Voltage control is critical for anodizing stainless steels. This is because chromium has two valence states, +3 and +6. Trivalent chromium forms an oxide film (Cr<sub>2</sub>O<sub>3</sub>) on the stainless steel surface. However, hexavalent chromium in the form of CrO<sub>4</sub><sup>2-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is very soluble in aqueous solutions. When an applied potential is higher than the potential producing hexavalent chromium, the oxide film on stainless steels will dissolve in the acid electrolyte. Therefore, anodic oxide films on stainless steels can only be produced in a certain range of potential or voltage. The current density is with positive and negative cycles. The positive and negative cycles of current

densities used are mentioned in Table (1).

The anodizing process for 304 stainless steel is examined with similar value of positive and negative cycles, no response was noticed.

At the beginning of the experiment, the applied current density was of similar value for positive and negative cycles, no response was noticed, then the value of current density was changed in the negative cycle to higher than that in the positive cycle, no response was noticed, and then the value of current density was changed in the positive cycle higher than that in the negative cycle, the response has been noticed. The above behavior can be explained as follows:

During the positive cycle, substrate material beneath the oxide film converts to oxide film and sulfides in the film are oxidized to a soluble species. During the negative cycle, trivalent iron is reduced to divalent iron and hydrogen gas is evolved. The negative cycle is specially designed to help remove ferrous oxide in the film since ferrous oxide is much more soluble than ferric oxide in aqueous solutions. Ferrous oxide and sulfides in the oxide film on stainless steel are determined to be major sources of localized corrosion [2].

Figure (3) shows SEM micrograph of anodized 304 stainless steel specimen surface. It contains dark spots which indicate that anodizing process dissolves the intermetallic particles in the solution as shown in Figure (3a). These spots are covered with oxide film formed. Anodic film hexagonal cells clearly appear in Figure (3b). The anodic film is thickening with increasing anodizing time as shown in Figure (3 c and d).

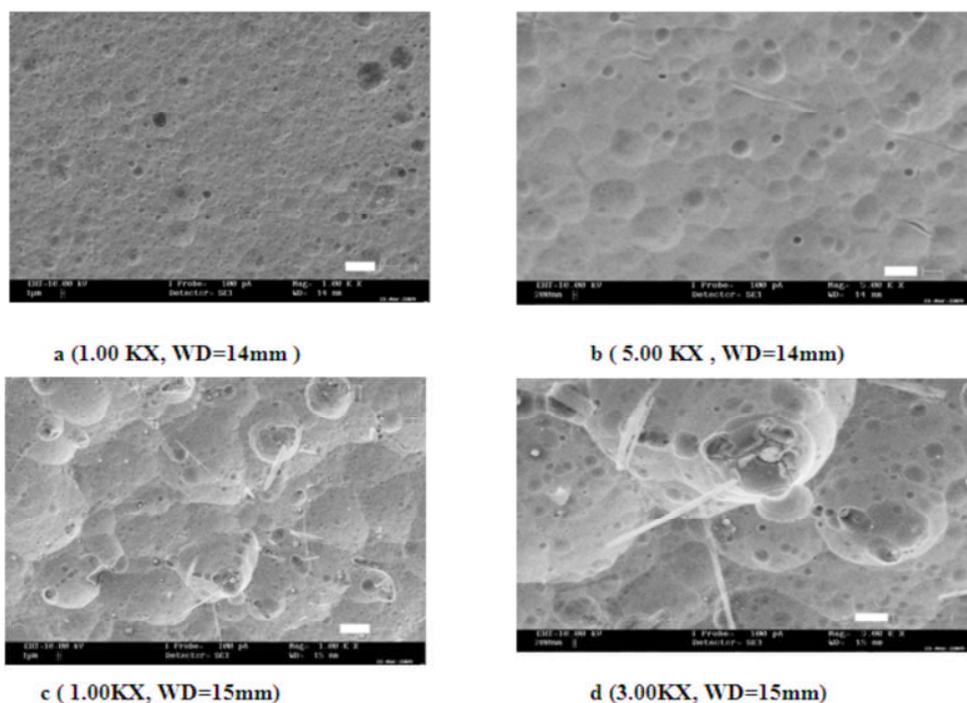


Figure 3. SEM micrographs for anodized 304 stainless steel specimens

During anodizing process, a little weight loss in this process is due removal of the iron ions from surface and this does not mean a complete removal, but there is a complex process of oxidation obtained for chromium and nickel in surface region, which has added the weight percent by the

addition of oxygen. It is generally noted little weight loss is natural and that the amount of iron removed is more than the amount of oxygen added to the elemental chromium and nickel to form their oxide.

Weight losses measurements are carried out at positive cycle (0.1- 0.2) A/cm<sup>2</sup> and negative cycle (0.01- 0.06) A/cm<sup>2</sup> at temperature (5 - 50) oC for time of (5-15) mins. The increase in weight loss was from 2.7514 to 2.7066g which is obtained under conditions of positive cycle of (0.1 A/cm<sup>2</sup>), negative cycle of (0.03 A/cm<sup>2</sup>), temperature of (10oC), and time of (10 min).

The loss in thickness by anodizing is calculated as:

$$\text{Reduced thickness} = 8.5 \text{ nm}$$

Figure (4-4) shows the X-ray diffraction phase analysis of the oxide layer on the 304 stainless steel specimens; the chart between intensity and 2- theta starts from 30o and end at 100o to the oxide film of the stainless steel type 304 specimens that was obtained in the experimental work, the black peaks indicate the raw material and the red peaks represent the nickel chromium oxide.

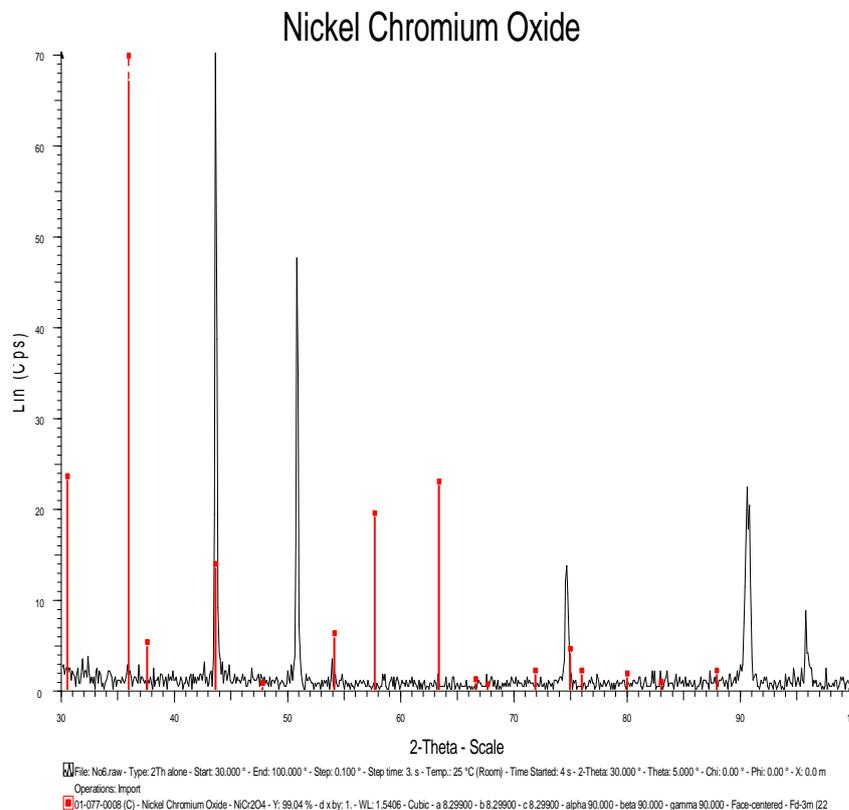


Figure 4. Nickel chromium oxide film

One can observe the appearance of the (NiCr<sub>2</sub>O<sub>4</sub>) oxide layer [9] and (FeNi) background [10] and (FeC) background [11]. The formation of (NiCr<sub>2</sub>O<sub>4</sub>) oxide layer was observed. Braggs Law is used to calculate d-spacing as shown in Table (3).

Table 3. The X-ray diffraction parameters; ( $2\theta^\circ$ ), d-spacing, phases, and (hkl) for anodized specimens.

$2\theta^\circ$	d(measured) $\text{\AA}^\circ$	d (standard) $\text{\AA}^\circ$	phases	(hkl)
30.50	2.93	2.104	NiCr <sub>2</sub> O <sub>4</sub>	004
36	2.50	2.492	NiCr <sub>2</sub> O <sub>4</sub>	211
37.50	2.40	2.397	NiCr <sub>2</sub> O <sub>4</sub>	202
43.70	2.08	2.062	NiCr <sub>2</sub> O <sub>4</sub> + FeNi+FeC	220
51	1.79	1.688	FeNi+FeC	312
54.10	1.70	1.705	NiCr <sub>2</sub> O <sub>4</sub>	204
57.80	1.60	1.598	NiCr <sub>2</sub> O <sub>4</sub>	303
63.30	1.47	1.472	NiCr <sub>2</sub> O <sub>4</sub>	224
75	1.274	1.273	NiCr <sub>2</sub> O <sub>4</sub>	305
90.50	1.085	1.199	FeNi+FeC	404
96	1.038	1.99	FeNi+FeC	404

The surface morphology after anodizing appears to be less smooth compared with electropolish specimen by using Atomic Force Microscopy (AFM) testing as shown in Figure (5a). It shows effective improvement in the surface characteristics due to building oxide layer on the surface. This conclusion agrees with (technical bulletin) studies [2].

Figure (5b), (5c) and (5d) shows that the values of (Ra) in the X, Y, and Z axes respectively are as follows:

- Figure (5 b) Ra =30.30 nm (X- axes)
- Figure (5 c) Ra =18.50 nm (Y- axes)
- Figure (5 d) Ra =27.60 nm (Z- axes)

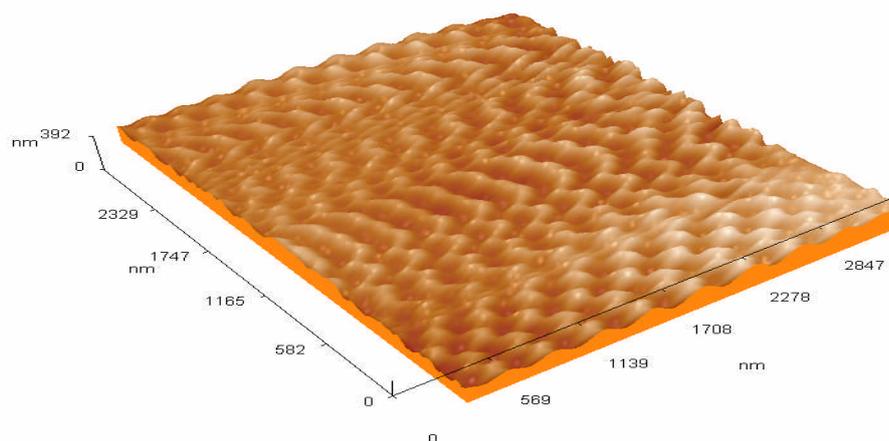


Figure 5a. The morphology of 304 stainless steel specimen after anodizing.

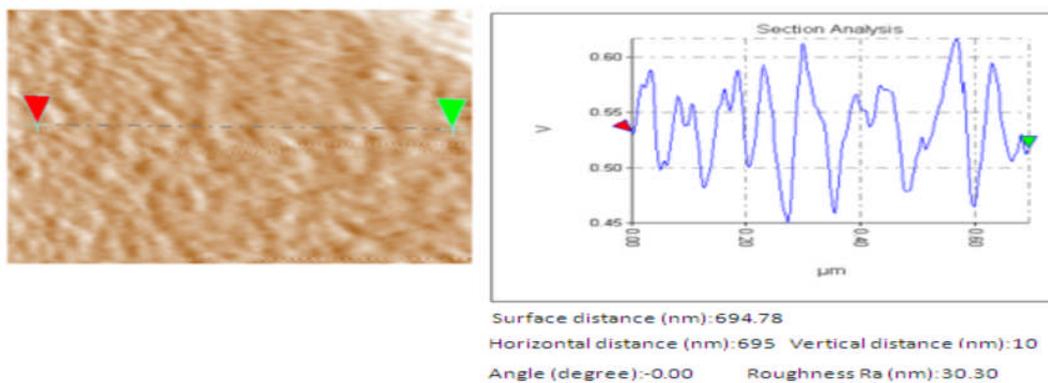


Figure 5b. Section analysis (X-axes).

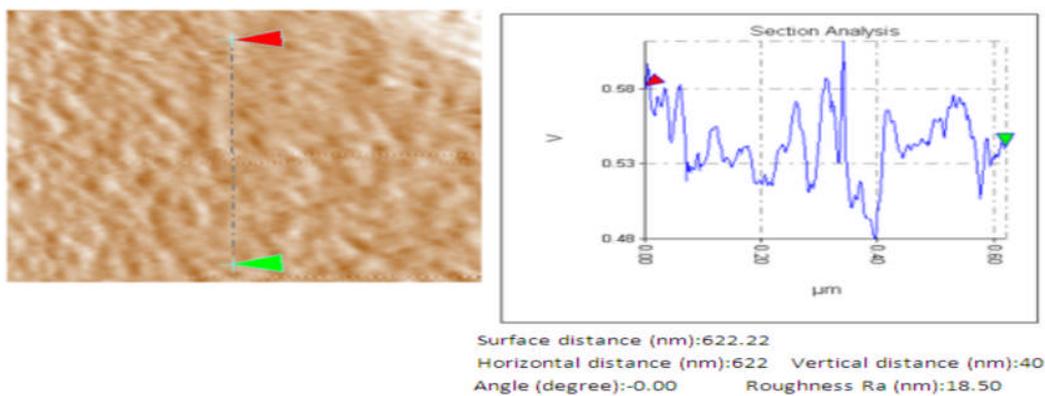


Figure 5c. Section analysis (Y-axes).

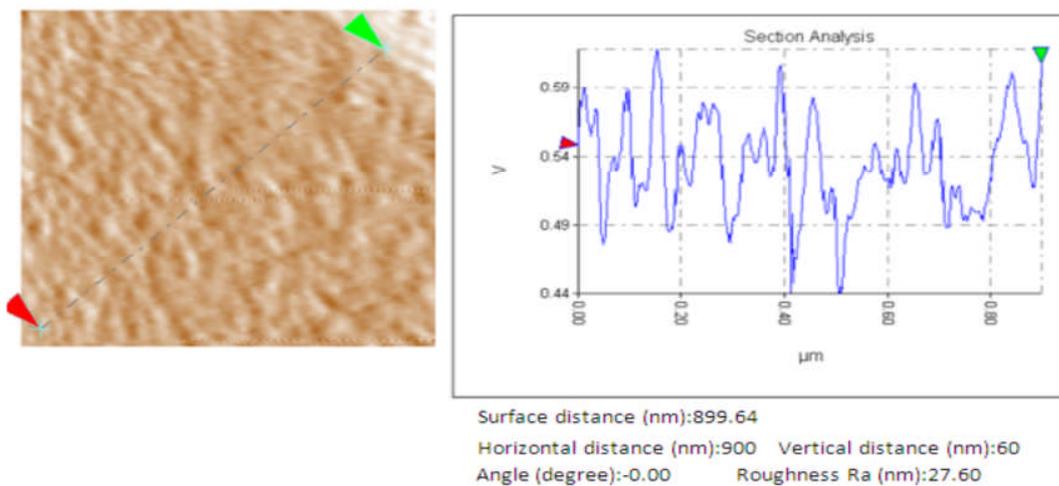


Figure 5d. Section analysis (Z-axes).

The hardness value was measured for anodizing specimen to be 158 Hv. Table (4) shows the hardness value for the untreated, electropolishing and anodizing specimens. The values of the hardness decrease with electropolishing and anodizing specimens respectively due to the increasing of chromium to iron ratio.

Table 4. The hardness of the untreated, electropolishing and anodizing specimens.

Process	Without treatment	Electropolishing	anodizing
Hardness (HV)	171	166	158

#### 4. Conclusion

For achieving efficient anodizing process on stainless steel type 304, electropolishing process should be applied before anodizing and it was observed that the best electropolishing conditions are current density of (0.55 A/cm<sup>2</sup>) at temperature of (95 oC) for time (10min.) which give the best brightness, smoothness. Anodizing process has been achieved successfully for first time locally on 304 stainless steel using an asymmetric power supply under conditions of current densities in positive cycle of (0.1 A/cm<sup>2</sup>), and negative cycle of (0.03 A/cm<sup>2</sup>), at temperature of (10oC), and time of (10 mins.). For anodizing 304 stainless steel, two current density cycles are applied. During the positive cycle, substrate material beneath the oxide film converts to oxide film and sulfides in the film are oxidized to a soluble species. During the negative cycle, trivalent iron is reduced to divalent iron and hydrogen gas is evolved. The negative cycle is specially designed to help remove ferrous oxide in the film since ferrous oxide is much more soluble than ferric oxide in aqueous solutions.

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