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ELECTROCHEMICAL MEASUREMENTS OF ANODIZING STAINLESS STEEL TYPE AISI 304

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ABSTRACT

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Stainless steels have surface passive layer which exhibits a truly remarkable property: when damaged (e.g. abraded), it self-repairs as chromium in the steel reacts rapidly with oxygen and moisture in the environment to reform the oxide layer. If the oxide forms a continuous layer on the surface it will stop or slow down the oxidation process and protect the metal from further corrosion. The oxide layer is enhanced with further thickening by anodizing process . This work deals with comparative study of corrosion behavior of mechanical polishing, electropolishing and anodizing 304 stainless steel specimens. Electrochemical measurements are applied using open circuit, polarization and cyclic polarization at room temperature in sea water (3.5% NaCl, pH 6.7). Improvement in corrosion resistance is clearly observed for specimens after anodizing process that shown, $E_{corr} = -359.6$ mV and $i_{corr} = 3.83 \mu\text{A}/\text{cm}^2$, while the specimen after electropolishing, $E_{corr} = -398.8$ mV and $i_{corr} = 4.69 \mu\text{A}/\text{cm}^2$, and specimen before treated, $E_{corr} = -419.9$ mV and $i_{corr} = 5.56 \mu\text{A}/\text{cm}^2$, and pitting potential increases in positive direction.

Keywords: Corrosion, Anodizing, Stainless steel 304, Electrochemical measurements

1. INTRODUCTION

Stainless steel 304 is the standard "18/8" stainless; it is the most versatile and most widely used, available in a wider range of products, forms and finishes than any other [1]. The corrosion resistance of austenitic stainless steels is primarily attributed to the passive oxide film formed on its surface that, exposed to an aqueous solution, is a mixture of iron and

chromium oxides, with hydroxide and water-containing compounds located in the outermost region of the film, and chromium oxide enrichment at the metal-film interface. However, the resistance of this passive film is determined by the environmental conditions which the stainless steel is exposed to, as well as by the alloy composition [3].

Wang et. al. [4, 5] investigated the corrosion behavior of colored stainless steel. The former characterized the pitting corrosion of colored samples obtained by chemical, INCO (chemical coloring + electrolytic hardening) and electrochemical (square-wave potential pulse) processes, using anodic polarization and electrochemical impedance spectroscopy in an HCl solution. Their experimental results showed that the pitting resistance of the colored samples increased in the following process order: chemical < electrochemical < INCO.

Pardo et. al. [6] pointed out that Mn and Mo were introduced in AISI 304 and 316 stainless steel composition to modify their pitting corrosion resistance in chloride-containing media. Potentiodynamic and potentiostatic polarization measurements are applied in 3.5 wt. % NaCl solution. A three-electrode cell was utilized, where the working electrode was the test material whereas the counter and reference electrodes were graphite and Ag/AgCl, respectively.

Potentiodynamic cyclic polarization measurements were performed at a scan rate of 0.5 mV/s, from –100 mV with respect to the corrosion potential (E_{corr}) and scanning back to the starting potential when the samples reached a current density value of $104 \mu\text{A}/\text{cm}^2$. On the other hand, potentiostatic measurements were performed to obtain the critical pitting temperature (CPT) applying a fixed potential of 0.25 mV and continuously increasing the electrolyte temperature at a rate of $0.16 \text{ }^\circ\text{C min}^{-1}$ until stable pitting occurs.

The passive film on stainless steel 304 remains relatively stable and the anodic reaction is under diffusion control. Pitting is a form of corrosion that produces relatively small pits, which are sometimes isolated or so close together to seem as rough surface. Pitting attracted much attention because it often leads to an extremely sudden failure and once pits initiate; they become capable of growing by self-sustaining mechanism. Pitting corrosion susceptibility depends on combination of alloy composition and environmental conditions since minor change in one of them may have major effect on both initiation and propagation of pits [7].

There is an urgent need to improve corrosion and pitting corrosion resistance of this type of steel using many recent techniques. The most recent technique method is anodizing process. Anodizing successfully combines science with nature to create one of the world's best metal finishes. It is an electrochemical process to produce an oxide film coating on metals or alloys for both protective and decorative purposes. The anodic coating is part of the metal, but has a porous structure which allows secondary infusion, (i.e. organic and inorganic coloring, lubricity aids, etc.). The anodic oxide films are mainly composed of chromium oxide and nickel oxide. Anodizing of stainless steels does not cause hydrogen embrittlement. The dimensions of parts will not change significantly [1, 8].

This paper investigates the corrosion behavior of mechanical polishing, electropolishing and anodizing 304 stainless steel specimens. Electrochemical measurements are applied using open circuit, polarization and cyclic polarization at room temperature in sea water (3.5% NaCl, pH 6.7).

2. EXPERIMENTAL PROCEDURE

2.1 Mechanical Pre-Treatment

Stainless steel type 304 (source Spain made) was received in the form of plate. Analysis of this plate was previously mentioned [2]. The plate was cut into small specimens into dimensions of (length*width*thickness) (4×1×0.1cm) and were used as specimens for electropolishing, anodizing and corrosion tests. They had sharp edges and then were chamfered via grinding wheel.

Prior to electropolishing, anodizing and corrosion tests, 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. HNO₃, 30% by vol. HCL, 30% by vol. glycerin and 30% by vol. and 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 [9]. Stainless steel 304 specimens were previously electropolished, then electropolished and anodized [2] to be used in electrochemical measurements.

3. ELECTROCHEMICAL MEASUREMENT

The electrochemical measurements were applied using computerized potentiostat shown in Figure (1). The electrochemical cell is 1-liter beaker capacity with magnetic stirrer inside the solution with a rotation speed of approximately 200(r.p.m.). The beaker solution was 3.5% sodium chloride at room temperature and around the beaker was a strip of aluminum which was used as an earth. The electrochemical cell consists of working, counter and reference electrodes. The counter electrode was made of platinum and was seated directly opposite to the working electrode. The reference electrode was a standard calomel electrode (SCE) bridged by a Luggin-Haber probe. The distance between the electrode surface and the Luggin-Haber capillary was set at about the optimum value of 1 mm. to minimize the experimental error due to IR drop.

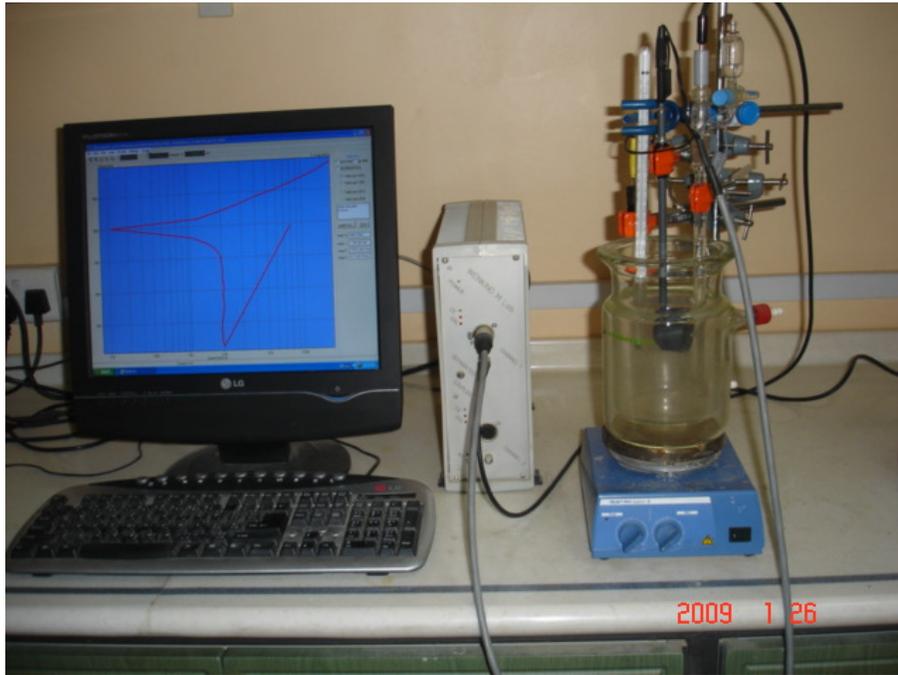


Figure (1) Electrical Corrosion Cell

3.1 Open Circuit Potential Measurements

After the supplying the cell of solution and electrodes. E_{corr} value was automatically recorded from instrument, till it reached a steady state value for about 30 minutes. This steady state value can be considered the actual E_{corr} in this environment.

3.2 Potentiostatic Measurement Procedures

Before any test, the one liter beaker was washed with tap water and followed by distilled water, then filled with test solution. Before any test, the auxiliary electrode was cleaned with distilled water and dried. The working electrode was immersed in the beaker solution about (5 Cm) from the solution surface.

After preparation of the working electrode, the corrosion cell parts were joined to each other and then connected to the potentiostat. The polarization began below the corrosion potential by about 250mV above E_{corr} . The polarization behavior curve was automatically printed. The cyclic polarization was applied to anodize and non-anodized specimens in the similar manner as to the above polarization specimens except the anodic behavior which continued until the break down occurred. Then, the potential decreased at the same sweep rate to reach the cathodic region.

3.3 Microstructure Examination

The microstructure evolution was investigated by means of optical microscope using microscope (Nikon-120, Japan) connected to the computer. The specimens were prepared from mechanical polishing, electropolishing and anodizing 304 stainless steel specimens after anodizing and also after polarization in 3.5 % NaCl solution to show the breakdown in the passive film and pitting formation.

4. RESULTS AND DISCUSSION

4.1 Corrosion Behavior

The corrosion behavior of conventional austenitic stainless steels was studied using open circuit, polarization and cyclic polarization tests at room temperature in sea water (3.5% NaCl, pH 6.7). These tests were done on unprotected, electropolishing and anodizing specimens.

4.1.1 General Corrosion Behavior of 304 Stainless Steel

Figure (2) shows several corrosion behaviors of 304 stainless steel specimens using Tafel extrapolation. This indicates cathodic and anodic regions. It also represents the relationship between current density and potential vs SCE for specimen without any treatment, $E_{corr} = -419.9$ mV and $i_{corr} = 5.56 \mu\text{A}/\text{cm}^2$.

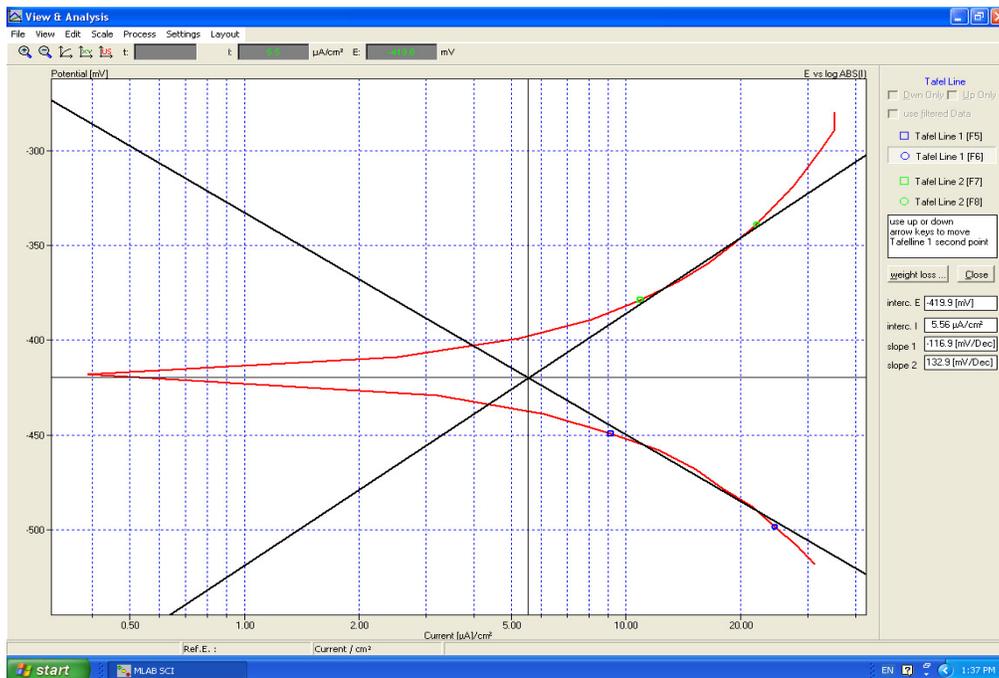


Figure (2) Polarization curve for specimen without any treatment

Figure (3) shows cyclic polarization curve for polarized specimen without any treatment. It shows cathodic and anodic regions and return to the cathodic region again. It also shows that at the anodic region, rapid increase in potential from critical potential $E_{corr} = -419$ until reaching 480 mV as breaking potential due to rapid increasing in current at this potential. Then potential decreases until it intersects the curve at repassivation potential $E_{rp} = -219$ mV. Then polarization curve shifts from primary curve as shown in Figure (3).

4.1.2 Corrosion Behavior of Electropolishing Stainless Steel

Figure (4) indicates the polarization curve for electropolishing 304 stainless steel which shows cathodic and anodic regions. The corrosion potential obtained is equal to -398.8 mV (SCE) and corrosion current density is $4.69 \mu\text{A}/\text{cm}^2$.

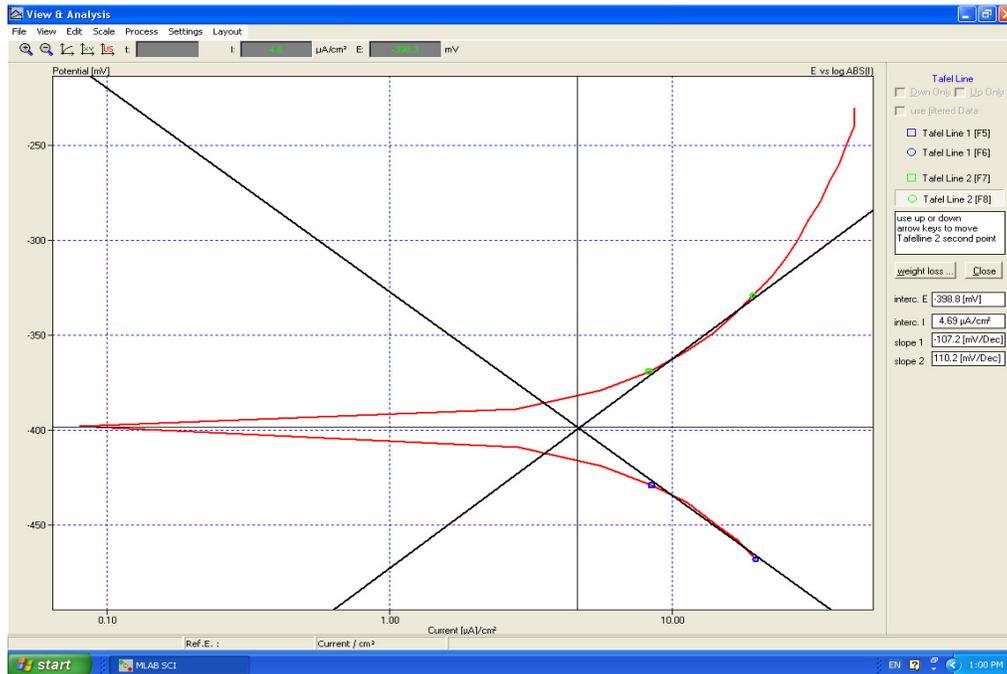


Figure (3) cyclic polarization for specimen without any treatment

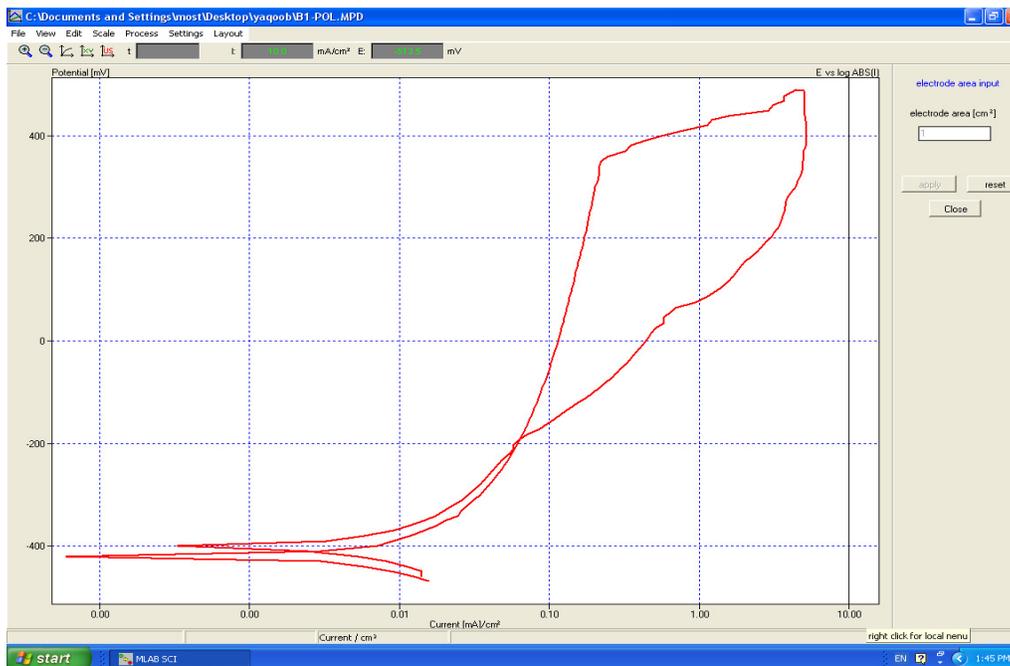


Figure (4) Polarization curve for electropolishing specimen

Figure (5) shows cyclic polarization curve for polarized electropolishing specimen. It shows cathodic and anodic regions and return to the cathodic region again. It also shows that at the anodic region, rapid increase in potential from critical potential $E_{corr} = -398.8\text{mV}$ until reaching 490 mV as breaking potential due to rapid increasing in current at this potential. Then potential decreases until it intersects the curve at repassivation potential $E_{rp} = -100\text{ mV}$. Then polarization curve shifts from primary curve as shown in Figure (5).

Prakash Sojitra et.al. [12] Proved that the quality of the surface of stainless steel is very much improved when subjected to electropolishing which improves corrosion resistance of stainless steel.

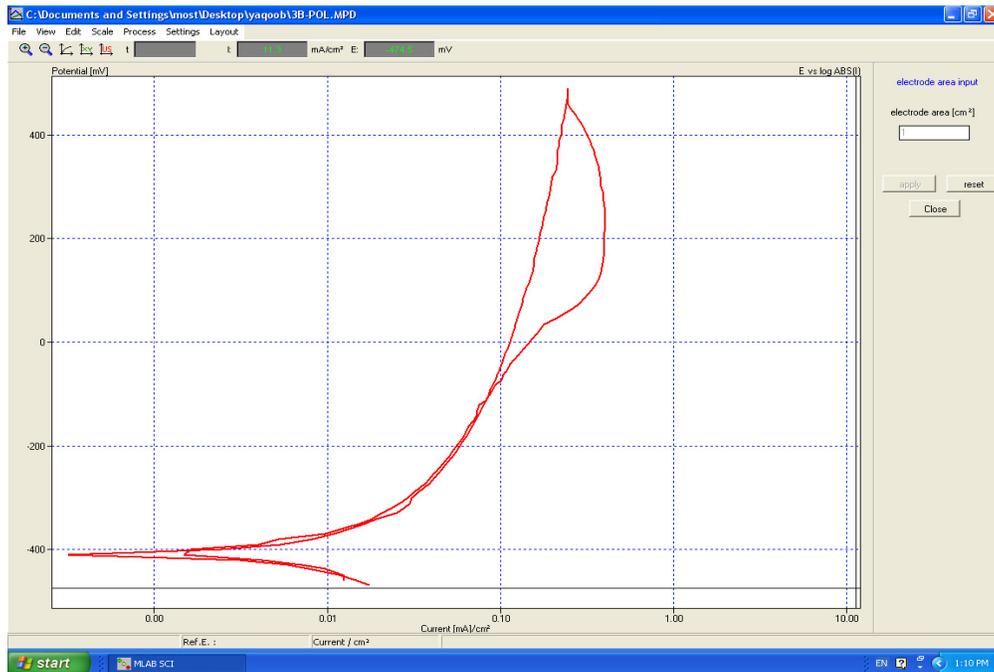


Figure (5) cyclic Polarization for specimen electropolishing

4.1.3 Corrosion Behavior of Anodizing Stainless Steel

Figure (6) indicates the polarization curve for anodizing 304 stainless steel which shows cathodic and anodic regions. The corrosion potential obtained is equal to -359.6 mV (SCE) and corrosion current density is $3.83\mu\text{A}/\text{cm}^2$.

Figure (7) shows cyclic polarization curve for polarized anodizing specimen. It shows cathodic and anodic regions and return to the cathodic region again. It also shows that at the anodic region, rapid increase in potential from critical potential $E_{corr} = -359.6\text{mV}$ until reachly 900 mV as breaking potential (pitting potential) due to rapid increasing in current at this potential and then potential decreases until it intersects the curve at repassivation potential $E_{rp} = -50\text{ mV}$. Then polarization curve shifts from primary curve as shown in Figure (7).

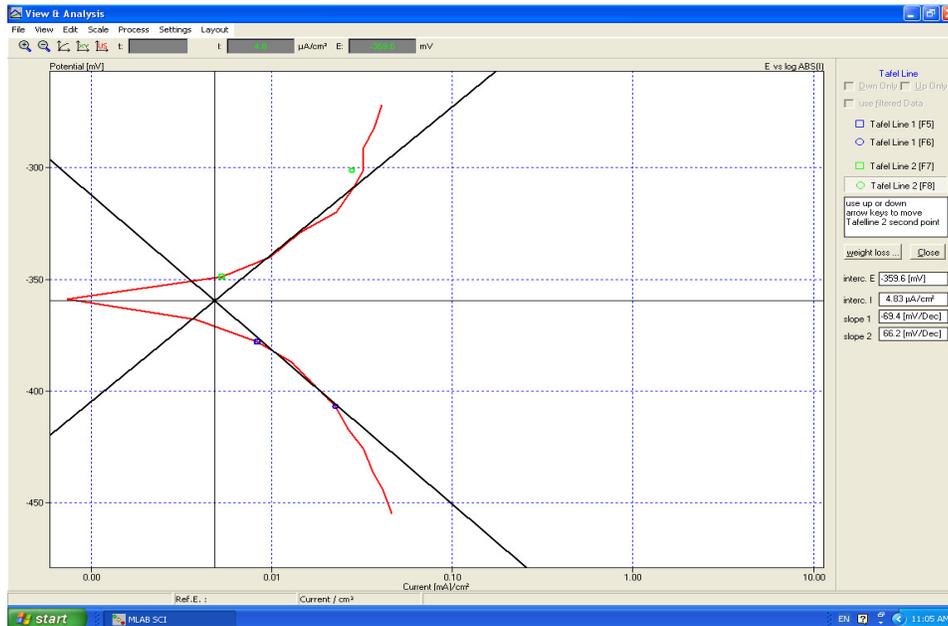


Figure (6) Corrosion behavior for specimen anodizing

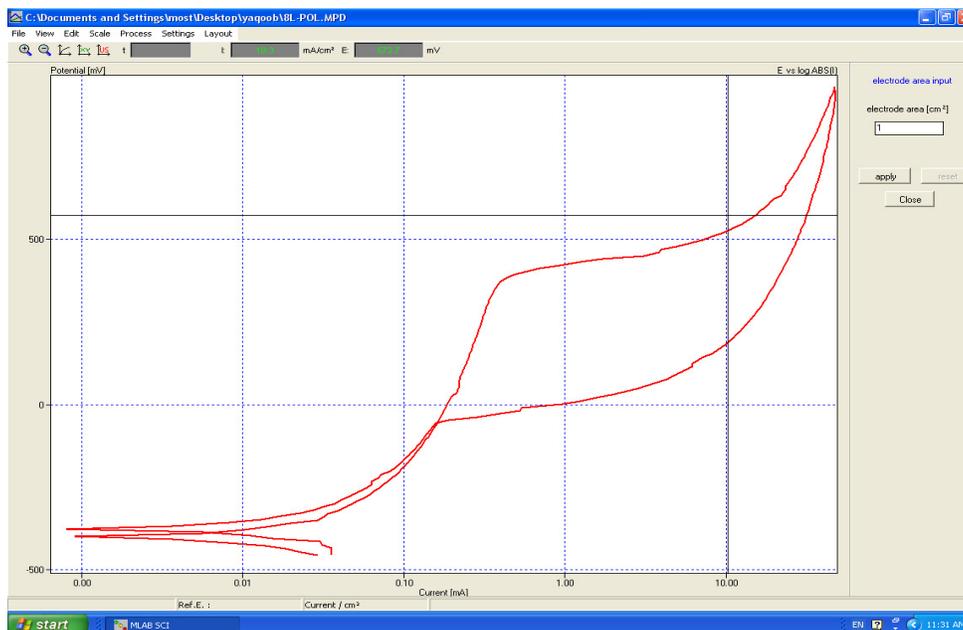


Figure (7) cyclic Polarization for specimen anodizing

Aniekan Etor,[13] , proved that the linear polarization resistance scan and potentiodynamic polarization scan are carried out along the crevice to measure the polarization resistance, R_p , and to obtain the passivity region along crevice of AISI 304 stainless steel but they do not yield good results. Low corrosion rate in the range of 0.06

mm/yr was calculated for the crevice of AISI 304 stainless steel, as compared with the results shown in table (1).

Table (1) shows the improvement in corrosion resistance as pitting potential increases from 480 mV to 900 mV, due to the formation of protection layer on the metal surface, this layer consists of nickel-chromium oxide as shown in Table (4-1). Burleigh,et.al. [14] Proved that the anodizing process for steel in KOH solution reduces the corrosion rate. These anodized oxides provide corrosion protection and they are also a suitable substrate for bonding organic coatings.

Table (1) The values of E_{corr} , i_{corr} , E_{rp} , E_b

specimens	E_{corr} , mV	i_{corr} , $\mu A/cm^2$	E_{rp} , mV	E_b , mV
Without any treatment	-419	5.56	-219	480
Electropolishing	-398.8	4.69	-100	490
Anodizing	-359.6	3.83	-50	900

4.1.4 Corrosion Rate Measurement

The calculated corrosion rate shown in Table (2) is according to the following equation [9]. Sample of calculations are:

$$CR \text{ (mpy)} = \frac{0.13 i_{corr} \times E.W}{A \times d}$$

Where:

i_{corr} = corrosion current, μA

E.W. = equivalent weight of the specimen = 25.24 g.equivalent [13].

d= density of specimen = 7.87 g. / cm^3 [13].

A: surface area =1 Cm^2 .

Table (2) illustrated the corrosion rate for untreated, electropolishing, and anodizing processes

Process	Untreated	Electropolishing	Anodizing
Corrosion rate (mpy)	2.3181	1.9553	1.5968

From Table (2), it is clear that corrosion rate for stainless steel 304 decreases with electropolishing and anodizing respectively. This is also, due to the formation of nickel-chromium oxide film on stainless steel. This agrees with study of Prakash Sojitra et.al. [12].

Figure (8) shows microstructure of specimen without any treatment after corrosion test. It indicates the presence of pits due to applied pitting corrosion and this means pit diameter value is about 43.85 μm .

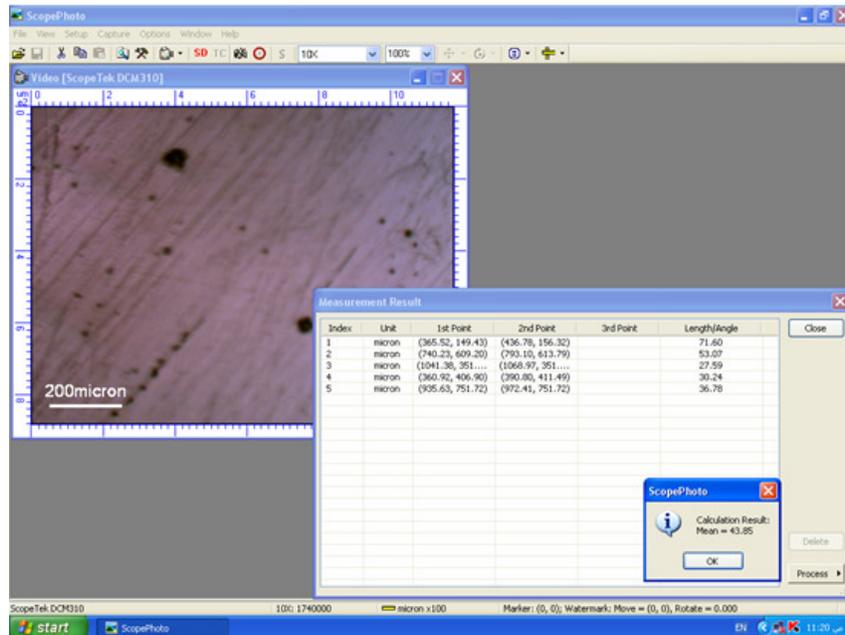


Figure (8) Microstructure of specimen without any treatment after corrosion test

Figure (9) shows microstructure of electropolishing specimen after corrosion test. The pit corrosion decreases compared with the bare specimen and that means pitting diameter value is about 25.96 μm .

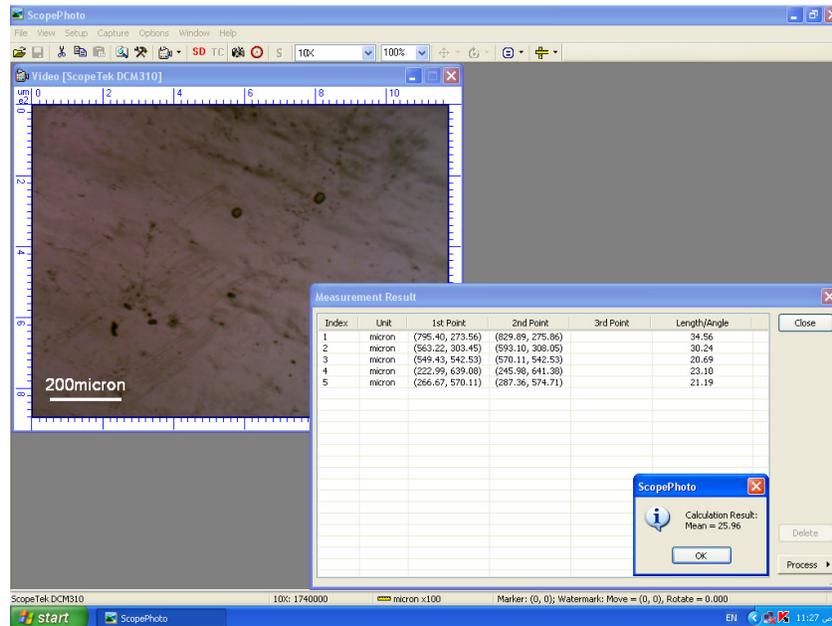


Figure (9) illustrated microstructure of electropolishing specimen after corrosion test

Figure (10) shows microstructure of anodizing specimen after corrosion test. The corrosion rate becomes less than before anodizing due to the presence of anodic oxide layer coated on the surface. This means pitting diameter value is about 21.29 μm .

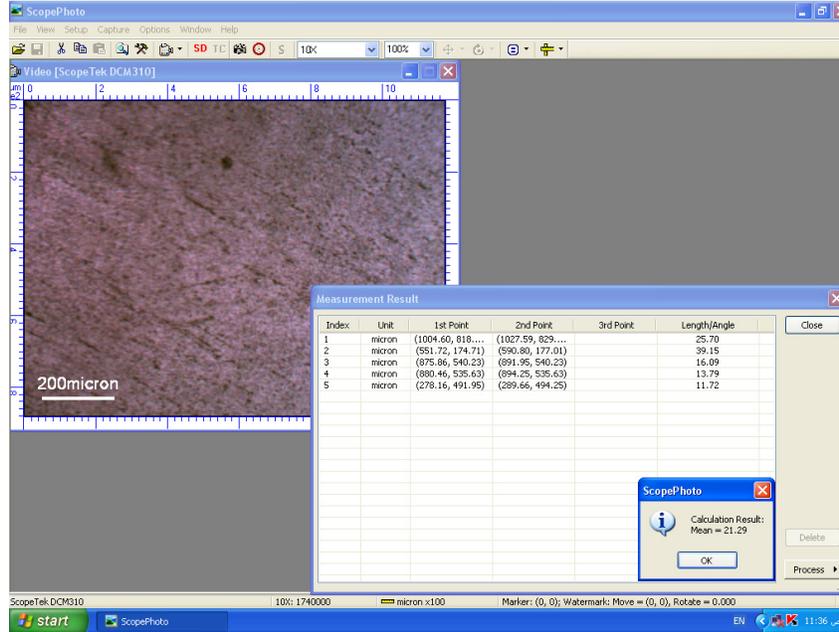


Figure (10) Microstructure of specimen anodizing after corrosion test

Table (3) indicates the highest resistance to pitting attack (i.e.) improvement in corrosion resistance after anodizing process.

Table (3) the mean pitting diameter

specimen	mean pitting diameter, μm
Without any treatment	43.85
Electropolishing	25.96
Anodizing	21.29

5. CONCLUSION

The corrosion potentials of electropolishing and anodizing specimens increase in positive direction. Corrosion current density decreases for treated specimens as follows:

$(i_{\text{corr}})_{\text{untreated}} > (i_{\text{corr}})_{\text{electropolishing}} > (i_{\text{corr}})_{\text{anodizing}}$; Due to the formation of nickel-chromium oxide layer.

Improvement in corrosion resistance is clearly observed for specimens after anodizing process by increasing chromium to iron ratio on the surface.

Pitting potential increases in positive direction as follows:

$(P_{\text{pit}})_{\text{untreated}} < (P_{\text{pit}})_{\text{electropolishing}} < (P_{\text{pit}})_{\text{anodizing}}$; This is also confirmed by mean pit diameter measurements which decrease in electropolishing and anodizing processes

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