

Studying the Corrosion Resistance of Anodized Low Carbon Steel in Alkaline Solution

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ABSTRACT

Low carbon steels are widely used materials in industrial application due to its availability and properties. Therefore it always needs to improve its properties especially corrosion resistance. One of the most important methods for improving its corrosion resistance is anodizing process. This study involves anodized of low carbon steels in 1 M sodium hydroxide (alkaline) electrolyte for 30 minute, using constant current technique at a range of (20-620) mA/cm².

Atomic force microscope (AFM) used to investigate the topography and anodic film parameters, it was found that the roughness of the anodic film is mainly depend on the anodizing current density and its increase from 0.9 (as polished) to (0.281-0.598) nm after anodizing. Coating thickness also increases with an increase in current density supply to the range of (2.5-13.3) μm. The corrosion behaviors of anodized and non-anodized of low carbon steel specimens in sea water are obtained. The corrosion current density and corrosion rate are decreased with an increase in anodic current density which increases anodic film thickness.

KEY WORDS: Anodizing, low carbon steel, constant current, polarization, corrosion.

الخلاصة

يستخدم الصلب الكربوني بشكل واسع في التطبيقات الصناعية لوفرتة وخواصه الجيدة، لذلك تبرز حاجة دائمية لتحسين خواصه وخاصة خواص التآكل. احد الطرق المهمة لتحسين مقاومة التآكل هي عملية الأنودة حيث تتضمن هذه الدراسة انودة الصلب الكربوني في مول واحد من محلول هيدروكسيد الصوديوم بزمان قدره 30 دقيقة باستخدام تقنية التيار الثابت بمدى 20-620 امبير/سم².

تم استخدام جهاز القوة الذرية (AFM) لدراسة طوبوغرافية سطح الأنودة، لقد وجد بأن خشونة طبقة الأنودة تعتمد بصورة رئيسية على كثافة تيار الأنودة حيث تزداد من (0.09 nm للمعدن الصقيل) الى (0.598 nm) بعد الأنودة. سمك التغطية يزداد كذلك مع الزيادة في كثافة التيار المسلط الى (13.3 μm). تم الحصول على سلوك التآكل للصلب الكربوني قبل وبعد عملية الأنودة باختلاف تيار التآكل حيث تم ملاحظة ان معدل التآكل يتناقص مع زيادة كثافة التيار الذي بدوره يزيد من سمك طبقة الأنودة.

INTRODUCTION

Low carbon steel is a low cost material with easy availability and excellent physical properties, these properties make it one of the best preferred materials for industry applications [1, 2]. The use of carbon steel means potential hazards are presented due to internal corrosion damage from aqueous produced fluids that contain acidic gases, carbon dioxide, and hydrogen sulfide [3].

The oxide film formed in passivation usually has a denser structure and higher chemical stability than bulk iron, therefore tends to mitigate further iron oxidation by preventing the direct contact between bulk iron and oxygen, hydroxyls and/or water molecules. Therefore, the multi-layer iron oxide film on steel surface is commonly referred to as the "protective layer" to reduce corrosion rate [5, 6].

Carbon flakes or nodules in iron or steel with high carbon content may cause an electrolytic potential and interfere with coating or plating ferrous metals are commonly anodized electrolytically in nitric acid, or by treatment with red fuming nitric acid, to form hard black ferric oxide. This oxide remains conformed even when plated on wire and the wire is bent [2]. The anodic film thus formed is composed of a compact inner layer and a porous outer layer and due to this porous structure; anodic film is susceptible to aggressive environments [7].

Burleigh et al. [8] investigated anodized steel in KOH solution to create an oxide layer on the surface of steel by using constant voltage technique, they found that at higher voltage and temperature, a semiadherent dichromic oxide is formed on the surface. The adherent oxide may be grown from nano to several microns thick on low carbon steel. These anodized film provide improved corrosion protection for steel and these are also suitable substrates for the bonding of organic coatings.

The aim of this work is to investigate the formation of anodic oxide film for low carbon steel by means of sodium hydroxide (as alkaline electrolyte) anodizing process with constant current; in terms of applied current, in order to study the effect of anodic coating on corrosion resistance.

EXPERIMENTAL

A sheet of low carbon steel with the chemical composition indicated in Table 1 was cut into specimens of dimensions of 2 cm× 2cm × 0.4cm. The surface of the alloy was ground using emery paper up to 1000 grit to produce a reasonably flat surface. Due to the very small depth of the field obtained from an optical microscope, it is essential that the surface is flat; in fact it needs to be optically flat acting as a perfect mirror. The specimen therefore has to be polished with 0.5 μm diamond paste. The specimens were carefully cleaned with water, rinsed with acetone and dried under air.

Figure 1 shows a typical microstructure of low carbon steel specimen of large ferrite phases as white areas and pearlite phases as dark areas. Analysis of these specimens was carried out using (spark technique) in (DC power supply RXN-3020D ELECTRONICS CO, LTD) as shown in Table 1. Stainless steel sheet type 316 with dimensions of (7x11x1 mm) was used as cathode.

To prepare anodized specimens, the specimens were ground in progressively fine silica water proof papers with grade of 120, 250, 350, 500, 1000 and 1200 grit. To remove the cold work from cutting and dust, grinding is carried out by hand; the specimen is rotated 90° and washing by distilled water between each step. After grinding, the specimens are finally polished using fine abrasives which have 1 micron diamond as a paste on red felt cloth.

The low carbon steel strip sample was connected to the positive terminal where it becomes (anode) while the stainless steel strip was connected to the negative terminal to be (cathode). The steel object and counter electrode are immersed in a solution of 1 mole NaOH in the anodizing vessel. Digital multimeter type (Victor 98 A) interface is connected to the desktop computer and power supply applying current density across the terminals to anodize the steel object by growing anodic oxidation film directly on a steel surface of the object.

The power supply is switched on in which current density increased gradually. Before the power supply is switched off, anode specimen is removed from anodizing cell immediately to prevent the dissolution of anodic film, then it's rinsed with running distilled water to remove the excess solution on the specimen. The sealing process is used when the anodizing process is completed, the

specimen is dipped in a flask filled with hot distilled water and kept for 20 minutes at 98 ± 1 oC to seal porous anodic film, and the specimens are drying at 60oC for 30 minutes.

AFM (Atomic Force Microscope) was utilized for surface characterization of porous anodic oxide film like porosity and roughness.

The polarization was carried out in a 1-liter beaker consisting of working, counter and reference electrodes. The working electrode was anodized and non-anodized carbon steel alloy, held by steel jigs designed to hold the specimens, it was covered with shrinkage tube to provide the bad contact and hold it stable in the cell. The counter electrode was a Pank type MLAB 200 seated directly opposite to the working electrode. The reference electrode was a standard calomel electrode (SCE) bridged by a Laggin-Haber probe. The distance between the electrode surface and the Laggin-Haber capillary was set at about the optimum value of 1 mm to minimize the experimental error due to IR drop; the polarization began below the corrosion potential about 250mV in cathodic region and then increased with sweep rate of 10 mV/ min. to the anodic region potentials. A thermometer was used to maintain the solution temperature within ± 1 oC at room temperature.

The corrosion current density is measured from polarization curve in order to use in corrosion rates calculations. Corrosion rates are calculated using the following relationship (9)

$$CR (mpy) = \frac{0.13 * I_{corr} * E.W}{\rho} \quad (1)$$

where:

I_{corr} : corrosion current, μA

E.W.: Equivalent weight of the specimen (28 g. / equivalent).

ρ : Density of specimen (7.81 g./ cm^3).

Results and Discussions

Anodized low carbon steel

Electrochemical anodizing was performed in 100 ml 1N NaOH by applying constant current density technique to get the response voltage against time. The appearance of the anodic oxide on low carbon steel sheet is related to the applied current densities.

The electrolyte is contained one mole sodium hydroxide. Figure 2 shows the response voltage with time at different applied constant current densities as shown in Table 2. The voltage tends to increase suddenly with anodizing time. Initially, anodic voltage values increase quickly with time then a voltage tendency to the steady – state value is distinguished for all cases in the range of 2.2 to 6.6 voltages. The steady state voltage reached in very short time which decreases with an increase in applied current density as shown in Figure 1. Coating thickness was measured using eddy current testing method (coating thickness gauge TT260 ITALY made), as shown in Table 2, the coating thickness increases with an increase in the current density due to the thick layer that precipitates on the low carbon steel surface.

Burleigh, et al. [1] indicated that an increase in anodizing voltage leads to increase the rate of growth of anodic film thickness.

Figure (3) shows the surface roughness of anodic film on low carbon steel, it can be concluded, after anodizing process the average roughness of low carbon steel was in the range of 0.281 to 0.598 nm respective to the applied current density. These values indicate that average roughness increases with an increase in applied current density as shown in table 2. The pore diameters for low carbon steel were measured as listed in Table (3).

The increase in applied current density leads to an increase in anodizing voltage which leads to an increase in growth rate in anodic oxide layer thickness resulting in an increase in surface roughness as shown in table (3). The pore diameter also decreases due to an increase in current density. This can be observed in the gradual increase in applied current density.

Linear polarization measurements of anodized and non anodized low carbon steel specimens in 3.5% NaCl solution are shown in figures (4-11). The polarization curves indicate the general behavior of cathodic and anodic regions. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) calculated using the tafel extrapolation method are also given in table (4). It is evident from table (4) that the increase in applied current density for anodized specimens decreases the i_{corr} and corrosion rates. The extent of decrease in i_{corr} and corrosion rates is found to be a function of the anodized applied current density, higher the applied current density, lower the values of corrosion rate and lower i_{corr} values.

The corrosion potential increases in the noble direction with the increase in anodizing applied current density. The observed positive shift (noble direction) in E_{corr} and the decrease in i_{corr} in the presence of anodic oxide layer (table 4) are conserved to be due to the nature of surface anodic oxide films on steel and suggest that the corrosion is under passive region control. It can be concluded from AFM results, that the pore size of anodic oxide film decreases with an increase in anodic applied current densities which improve corrosion resistance of low carbon steel as shown in table(4).

Conclusions:

The following conclusions can be drawn from this study:

- 1- The roughness of anodic film increases with increasing anodizing current density.
- 2- The thickness of anodic film increases with increasing anodizing current density.
- 3- The pore diameter of the anodized surface is decreases with an increase in current densities.
- 4- Improvement in corrosion resistance is clearly observed for specimens after anodizing process due to increasing the thickness of anodizing layer.
- 5- Corrosion current density decreases for anodizing specimens compared with non-anodizing.
- 6- The corrosion potential increases to noble direction due to increase in anodized current densities.

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Table (1): Standard and analytical chemical compositions of low carbon steel alloy.

Metals	Iron	Carbon	Manganese	Aluminum	Copper	Sulfur	Phosphorus
Standard by ASTM A568	Rem.	0.02-0.07	0.35 max	-	-	0.035 max	0.030 max
Analysis by (wt.%)	99.67	0.07	0.21	0.03	0.02	-	-

Table (2): Anodizing voltage and coating thickness at different current densities supply.

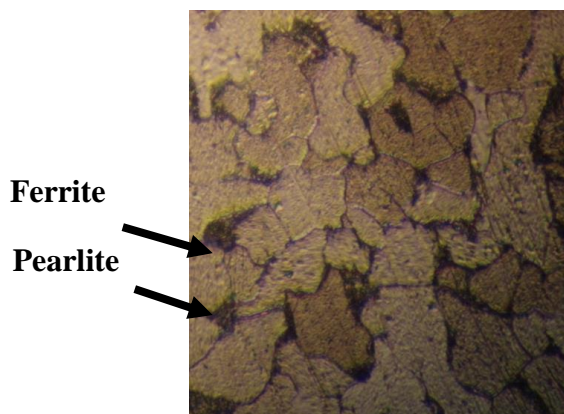
Sample No.	Current density supply (mA/cm ²)	Voltage V	Coating thickness μm
0	-	-	-
1	20	2.2	2.5
2	120	3.7	2.7
3	220	4.4	4.7
4	320	4.6	4.8
5	420	6.1	5.3
6	520	6.4	6.5
7	620	6.6	13.3

Table (3): Anodic layer specifications by AFM contact mode

No	Current density mA/cm ²	Roughness average nm	Average pore diameter nm	Pore depth nm
as	-	0.09	-	-
1	20	0.281	166.37	0.833
2	120	0.304	165.66	0.882
3	220	0.304	159.82	0.858
4	320	0.383	128.27	1.16
5	420	0.393	101.57	1.18
6	520	0.404	89.47	1.24
7	620	0.598	84.95	1.8

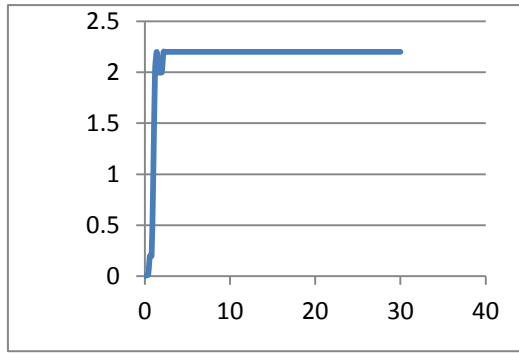
Table (4): corrosion rate of anodized carbon steel at different current densities.

Sample No.	Current density supply (mA/cm ²)	I _{corr.} (μA/cm ²)	E _{corr.} (mV)	Corrosion rate (mpy)
0	-	15.19	-539.5	7.081
1	20	2.12	-359.7	0.988
2	120	2.07	-341.3	0.965
3	220	1.75	-368.8	0.816
4	320	1.19	-351.6	0.555
5	420	1.05	-342.9	0.489
6	520	0.636	-305.9	0.296
7	620	0.376	-279.5	0.175

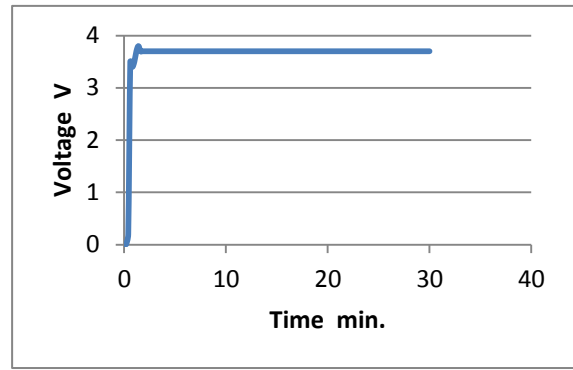


X750

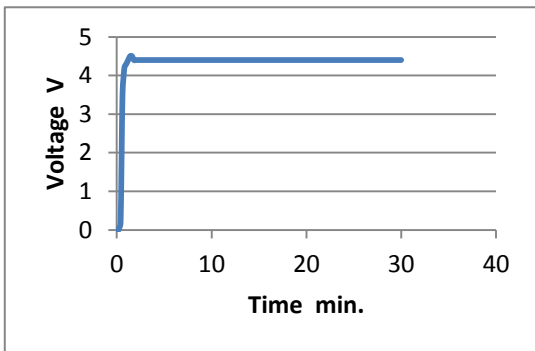
Figure (1): Microstructure of low carbon steel polished and etched with natal solution for 1 min



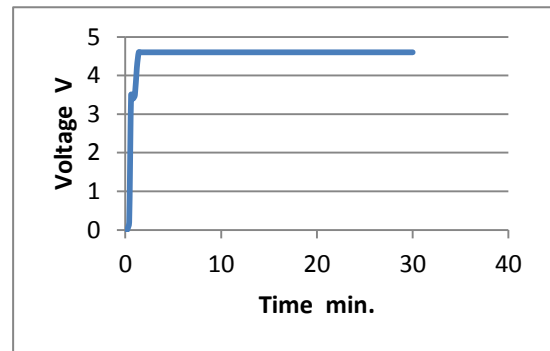
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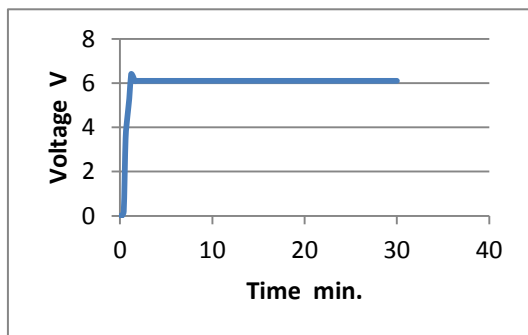
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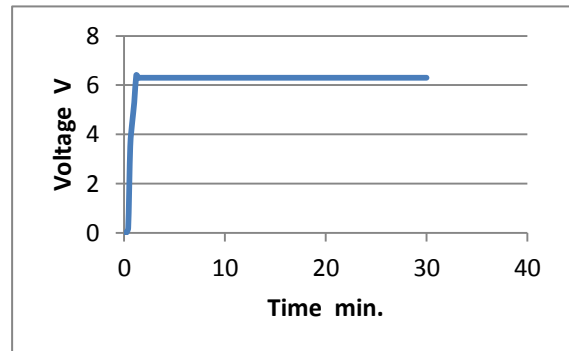
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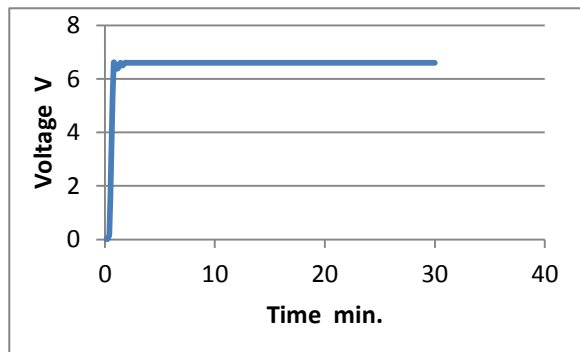
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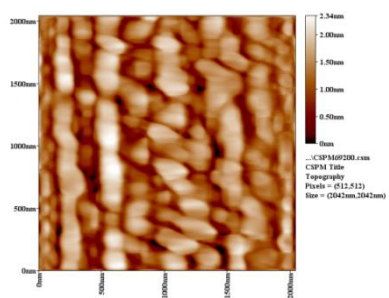


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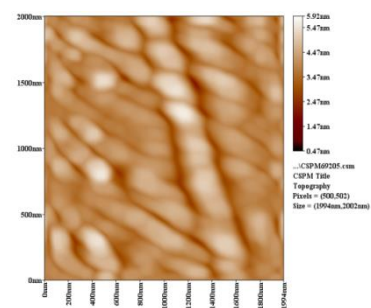
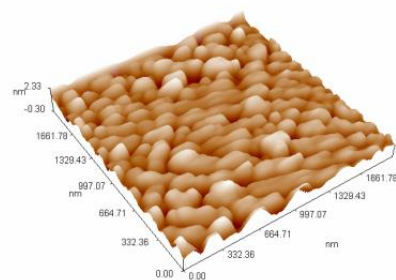


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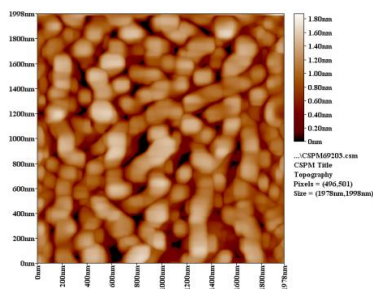
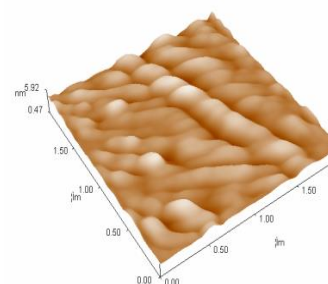
Figure (2): relationship between voltage and time at different current densities: a-20, b-120, c-220, d-320, e-420, f-520, g-620 mA/cm².



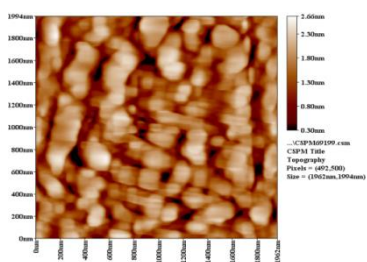
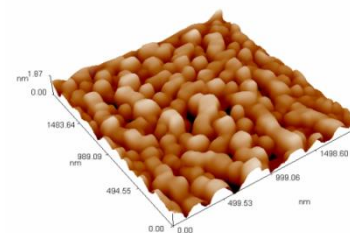
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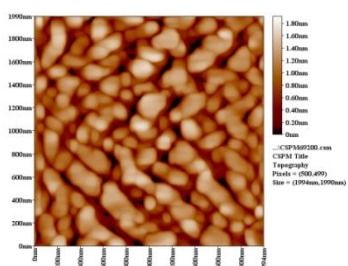
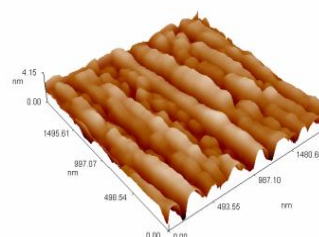
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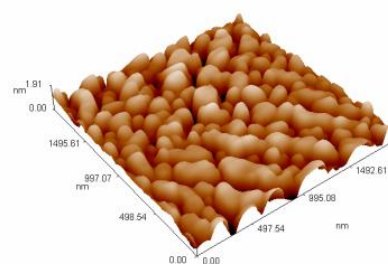
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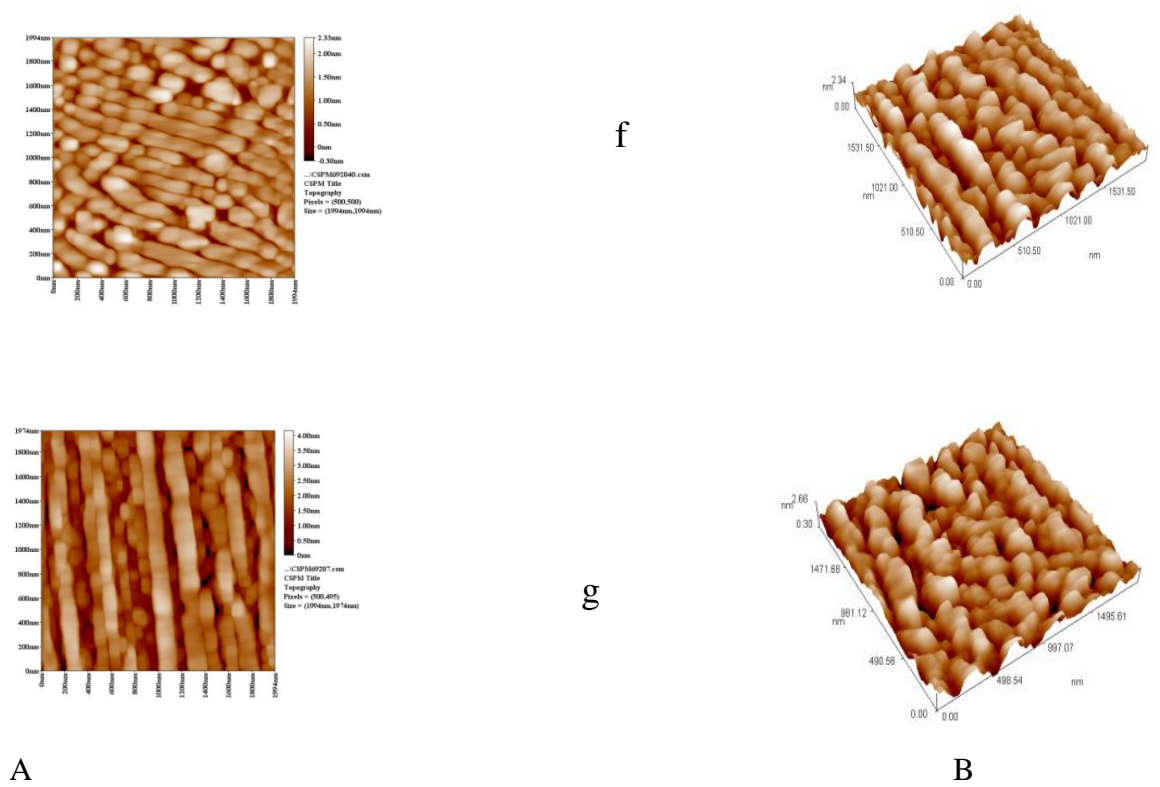


Figure (3): AFM contact mode for anodized carbon steel at different current densities: a-20, b-120, c-220, d-320, e-420, f-520, g-620 mA/cm², (A) 2D, (B) 3D.

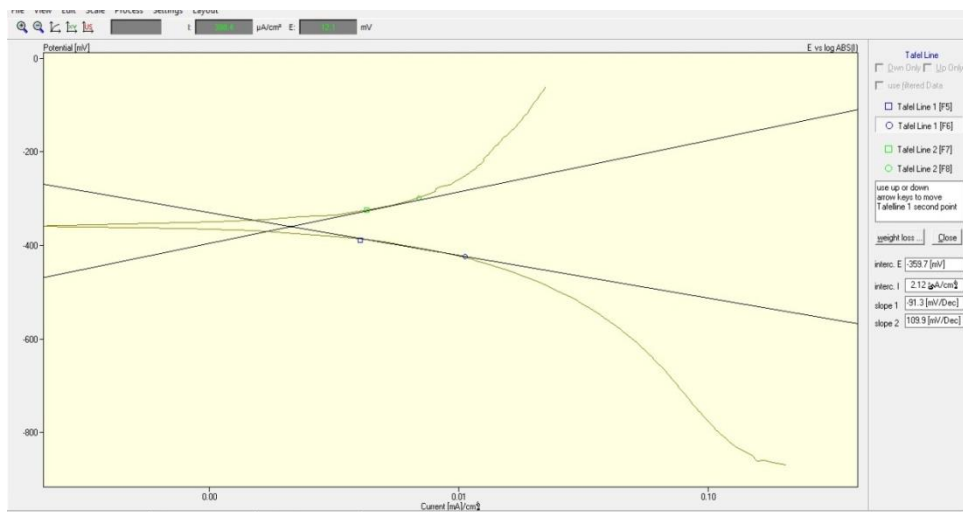


Figure (4): corrosion behavior of anodized low carbon steel at current density of 20 mA/cm²

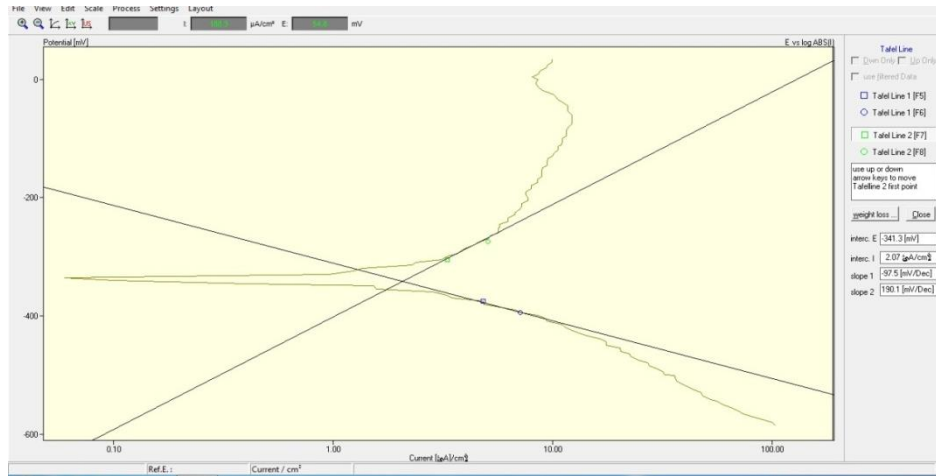


Figure (5): corrosion behavior of anodized low carbon steel at current density of 120 mA/cm²

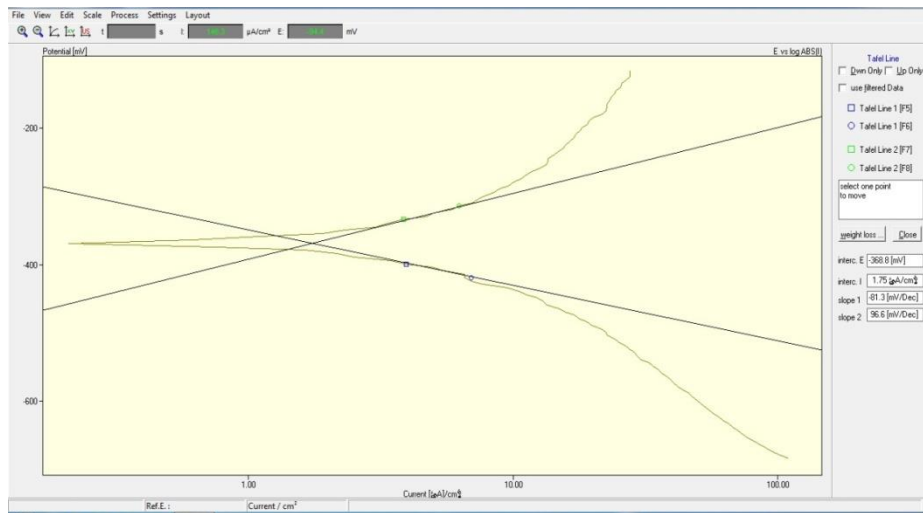


Figure (6): corrosion behavior of anodized low carbon steel at current density of 220 mA/cm².

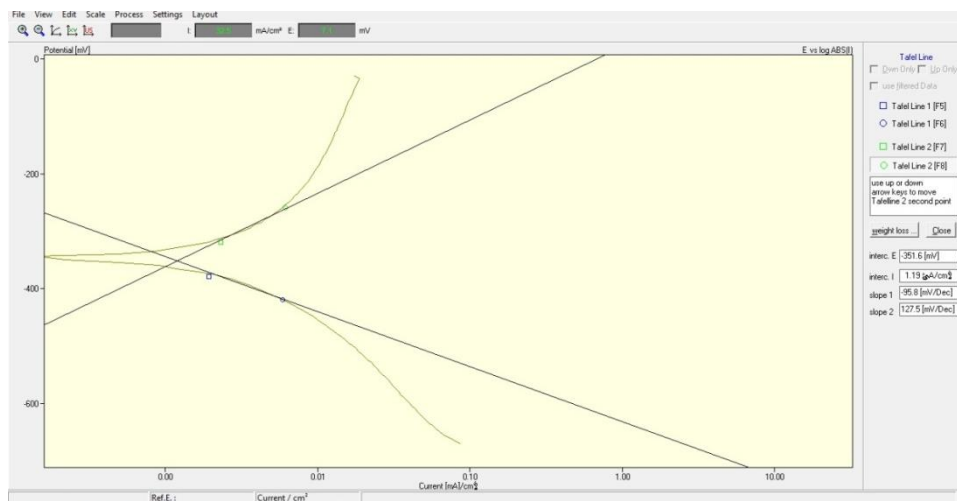


Figure (7): corrosion behavior of anodized low carbon steel at current density of 320 mA/cm².

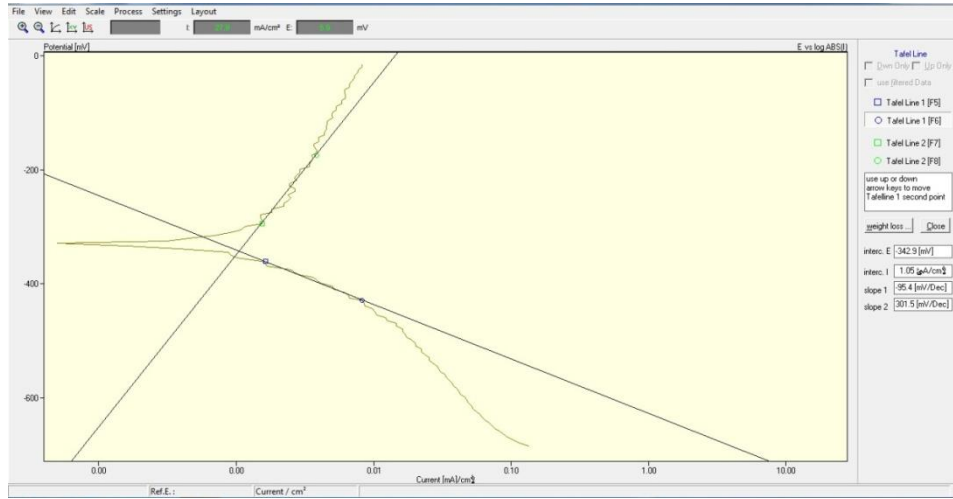


Figure (8): corrosion behavior of anodized low carbon steel at current density of 420 mA/cm².

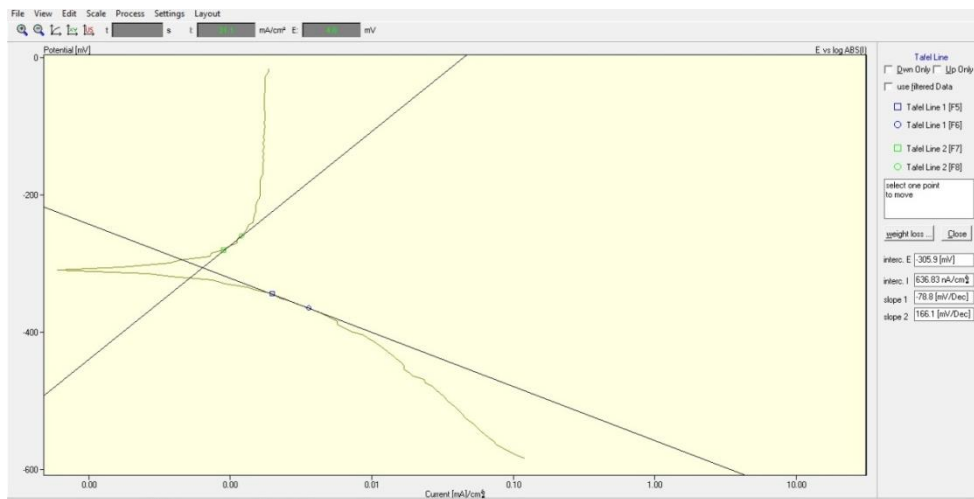


Figure (9): corrosion behavior of anodized low carbon steel at current density of 520 mA/cm².

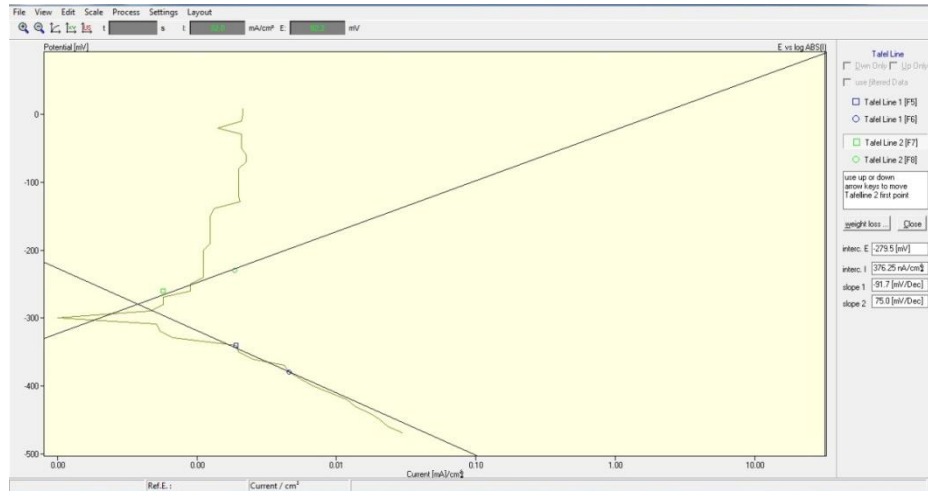


Figure (10): Corrosion behavior of anodized low carbon steel at current density of 620 mA/cm².

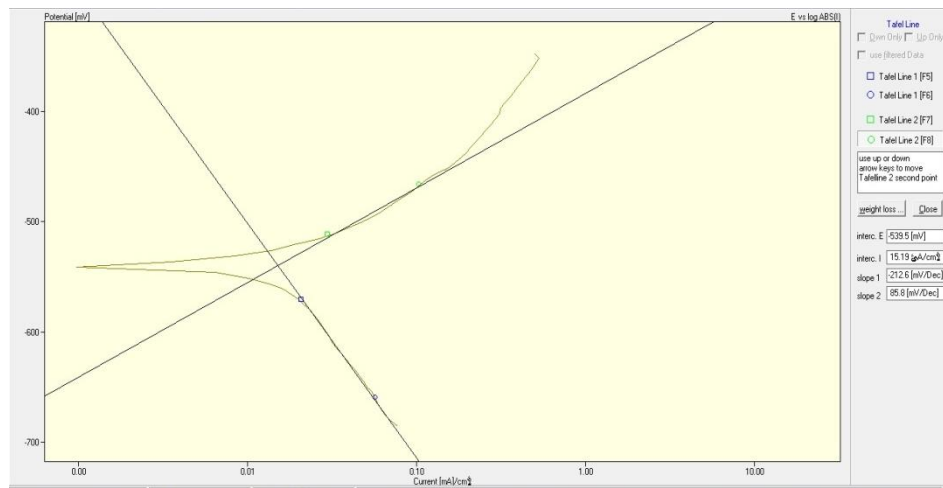


Figure (11): corrosion behavior of low carbon steel before anodizing.