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Heat Treatment Effect on Anodizing Corrosion Resistance of Low Carbon Steel

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Abstract

This work involves studying heat treatment effect on anodized low carbon steel using electrochemical measurements. Heat treatments of low carbon steel before anodizing were applied by anodizing at different temperatures of 650, 900, and1000°C for one hour. Anodizing process was used for non-annealed and annealed low carbon steel at the above temperatures in KOH solution.

The electrochemical behavior of low carbon steel, anodized low carbon steel, and anodized annealing low carbon steel at the above temperatures in 3.5 wt% NaCl solution using potentiostat device. Corrosion rates for the above conditions were measured. The corrosion rates measured results indicate an improvement in corrosion resistance of anodized annealing low carbon steel. Surface characterization of anodic film on low carbon steel was examined anodic film on low carbon steel using Atomic force microscopy (AFM) and optical microscopy used to examine the specimens before and after corrosion test. the practical results indicate the best conditions to obtain higher corrosion resistance are for anodized low carbon steel annealed the steel before anodizing at 1000 °C.

Keywords: Corrosion rate, anodizing process, Atomic force microscopy.

1. Introduction

During the last two decades, methods of surface engineering processes have been developed to enhance the wear resistance, hardness, and corrosion performance of materials [1].Corrosion of reinforcing steel is common in reinforced concrete structures around the world. It causes premature deterioration of civil infrastructures such as highway and railway bridges, offshore platforms, pipelines, and dams. According to Koch et al. [2], the annual cost of corrosion in the United States is approximately $8 billion for highway bridges alone. Corrosion of reinforcing steel in concrete results from two main sources: carbonization and chloride penetration. Chloride mainly comes from road deicing salts in winter for highways and bridges, and marine climate for offshore and coastal

structures. One effective way to prevent or slow down the penetration process of these aggressive ions is to apply a coating on the rebar surface that would establish a physical barrier layer between the steel and concrete [2].

Corrosion is defined as the destruction or deterioration of material because of reaction with its environment. This definition should be restricted to metals, but often the corrosion engineers must consider both metals and nonmetals for solution of a given problem. . Corrosion resistance and mechanical properties are usually the most important factors in the selection a grade for a given application [3].

Corrosion behavior of different carbon steel materials in different media typical of the in-service environments has also been investigated by many researchers. The acidic environments are generally en- countered in many industrial processes. Acid solutions are used especially for the removal of undesirable scales and rust from carbon steel materials , particularly, hydrochloric acid is widely used for the picking processes of metals [4]. Corrosion behavior of numerous grades of carbon steels in hydrochloric acid solutions has been widely studied by many researchers [5-10].

The electrolytic passivation process is used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called “anodizing” because the part to be treated forms the anode electrode of an electrical circuit. Anodizing increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than bare metal [11]. Anodization changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance [11].

2- Experimental:-

2-1 Anodized of Low Carbon Steel

Low carbon steel metal was used in this study It's chemical composition is presented in Table 1.

Table 1: Chemical Composition of Low Carbon Steel (wt %).

C%	si%	Mn%	P%	S%	Cr%	Mo%	Ni%	Al%	Co%	Cu%	V%	Fe%
0.102	0.007	0.528	0.007	0.003	0.007	0.011	0.035	0.068	0.005	0.20	0.002	Bal.

Anodization was carried out in (15g KOH + 100 ml distilled water) at 15 volts for 15 min at room temperature. The low carbon steel to be anodized was connected to the positive the anode of the power supply and a stainless steel counter electrode was connected to the negative electrode at the power supply as the cathode. . The specimens before anodized annealed, the annealed was done at different temperatures (650, 900, and 1000) °C for 1 h. In order to reduce residual stresses developed during fabrication and used protective atmosphere furnace by nitrogen gas [11]. Atomic-Force Microscopy (AFM) study was carried out by (220V, AA3000, Angstrom Advanced Inc. USA) which was utilized for morphological and structural characterization. The computerized optical microscopy (Type MeF) and digital camera was used to examine the microstructure of all specimens. After anodization, the specimens were rinsed in deionized water, then rinsed in methanol, and dried by air using compressed air. Coating thickness was measured using eddy current testing method (coating thickness gauge TT260 ITALY made),

2-2 Electrochemical Measurements

The electrochemical techniques are used to study the corrosion behavior of materials. In electrochemical studies, samples were immersed in 3.5 wt. % salt solution. Samples were tested at room temperature with a typical three-electrode setup, including a (100 mm × 10 mm) platinum rod as a counter electrode, saturated calomel electrode (SCE) as a reference electrode, and the test specimen as a working electrode. All three electrodes were connected to a potentiostate (WENKING M lab multi channels and SCI-M lab corrosion measuring system from Bank Electronic-Intelligent controls GmbH Germany) . For the potentiostat polarization experiment, the test was conducted at a scanning rate of 2 mV/s.

Corrosion current density (i_{corr}) was determined from polarization curves by Tafel extrapolation .The corrosion rate in milli-inches per year (mpy) can be determined from following Equation [11].

$$\text{Corrosion Rate (mpy)} = \frac{0.13\, i_{corr} * (E.W)}{d}$$

Where
mpy= milli-inches per year
i_{corr}=corrosion current density (μA/cm^2)
E.W=equivalent weight of the corroding species, (g).
d = density of the corroding species, (g/cm^3).

3- Results and Discussion:-

3-1Morphology of Anodic Oxide Films

Annealing is a generic term denoting a treatment that consists of heating to and holding at a suitable temperature followed by cooling at an appropriate rate (normally very slow cooling), primarily for the softening of metallic materials [12]. Figure 1 shows optical micrographs for the microstructure of the cross sectional uncoated and coated samples before corrosion tests for low carbon steel. The microstructure of the as-received material (Figure 1a) consisted of pearlite colonies (dark contrast) and ferrite grains (light contrast). Figure 1b. Shows microstructure of low carbon steel annealed at 650°C which consists of the ferrite and pearlite grains and stress relief is occurred for this specimen. (Figure 1c) indicates different structure morphologies during heating the steel to 900°C, by increasing the ferrite and austenite areas. During an intercritical annealing, the recrystallization of ferrite and forming of austenite are preceded. Figure 1d indicates the different structure morphologies during heating the steel to 1000°C. In the Figure 1d, the black patches represent the pearlite structures while the seemingly white patches represent the ferrite structures. The amount of ferrite and austenite and other precipitates were measured using optical and image analyzer

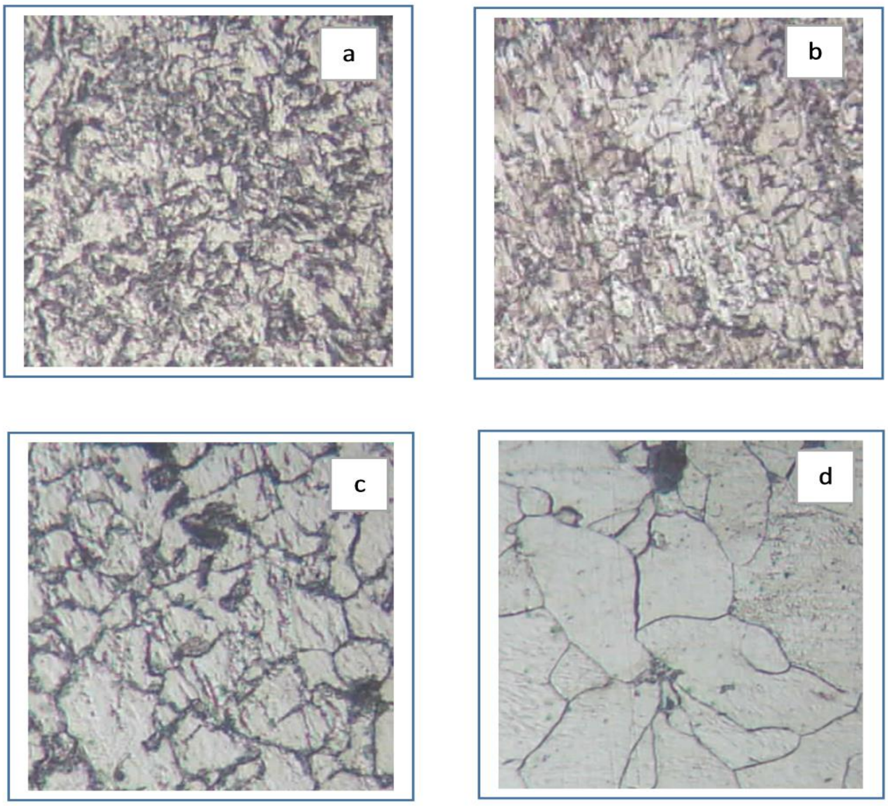


Figure 1: Optical micrographs showing the microstructures of low carbon steel (a) as-cast, (b) annealed 650°C, (c) annealed 900°C, (d) annealed 1000 °C.

The results revealed that the ferrite percentage increased as the heating temperature increase [13]. Effect of annealing temperature on the microstructure of low carbon steel is shown clearly in figure 1. One can be seen from Figure1 that the grain size becomes larger as the annealing temperature increases, this due to lower cooling rate. Annealing, normalising, hardening and tempering are the most important heat treatments often used to modify the microstructure and mechanical properties of engineering materials particularly steel [13] . Atomic-Force Microscopy (AFM) was used to examine the anodized low carbon steel surfaces. The low carbon steel was covered with oxide layers fabricated by anodization process as shown in Figure (2) which illustrates the case of anodizing low carbon steel at 15V without annealing. The pore sizes of anodizing low carbon steel is (72 nm), and anodic film thickness is 2.7 µm

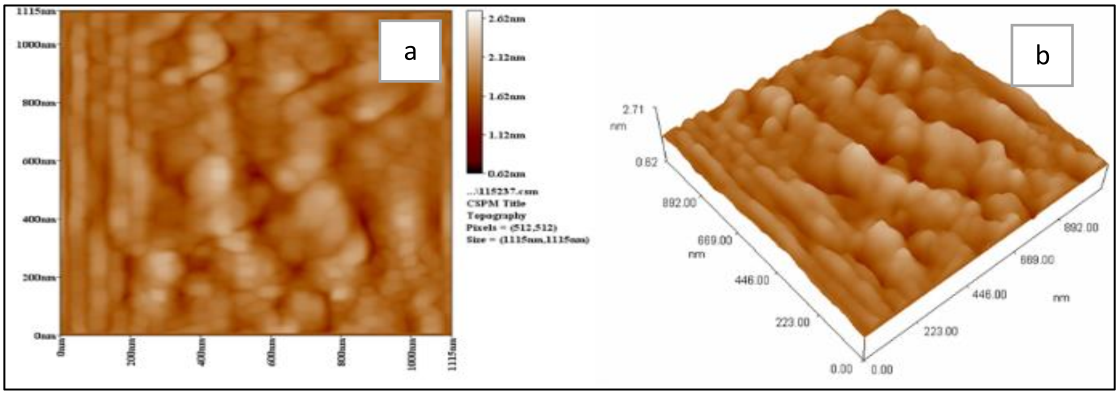


Figure 2: AFM Surface scan of anodized low carbon steel without annealing
a. (2D) View, b.(3D) View

Figures (3 to 5) show that surface topography of two dimensional (2D) and cross-sections of anodizing low carbon steel are formed at anodizing potential of 15 V with annealing at different temperatures (650, 900, and1000) °C for 1 h, respectively. The average pore sizes are (58.24 nm, 52.70, and 52.30 nm) respectively. The decrease in the average pore sizes is due to higher annealing temperature. The anodic film thickness for annealed specimens at (650, 900, and 1000°C) are, (3.3, 5.7 and 12.2 μm) respectively

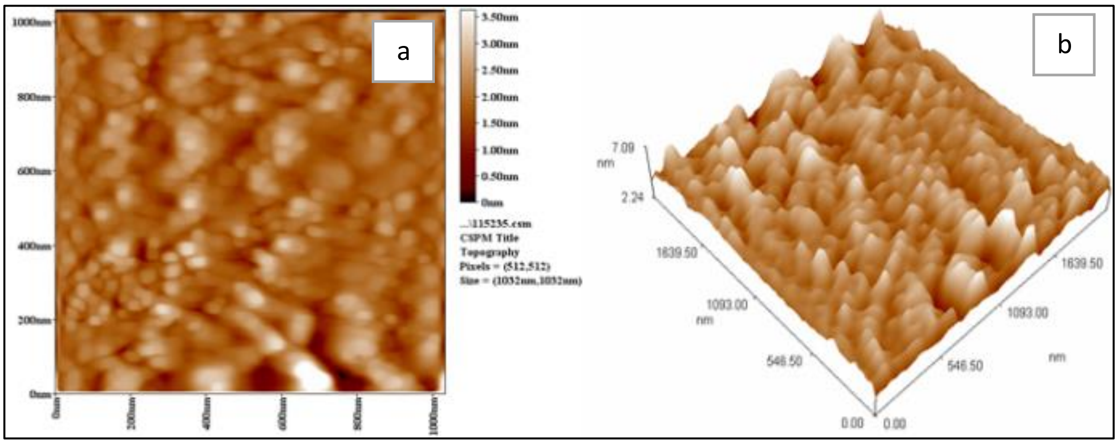


Figure 3: AFM Surface scan of anodized low carbon steel at annealed 650°C a. (2D) View, b.(3D) View.

These results indicate that the anodic film thickness increase with increasing annealing temperature and low pore size. This illustrates that annealing process relief the internal stresses present in the specimens and soften the material with grain growth. This is clearly observed in Figure 1 d for annealed specimen at 1000°C compared with other specimens. These observations increase anodizing response which increase anodize film thickness and reduce the pores size.

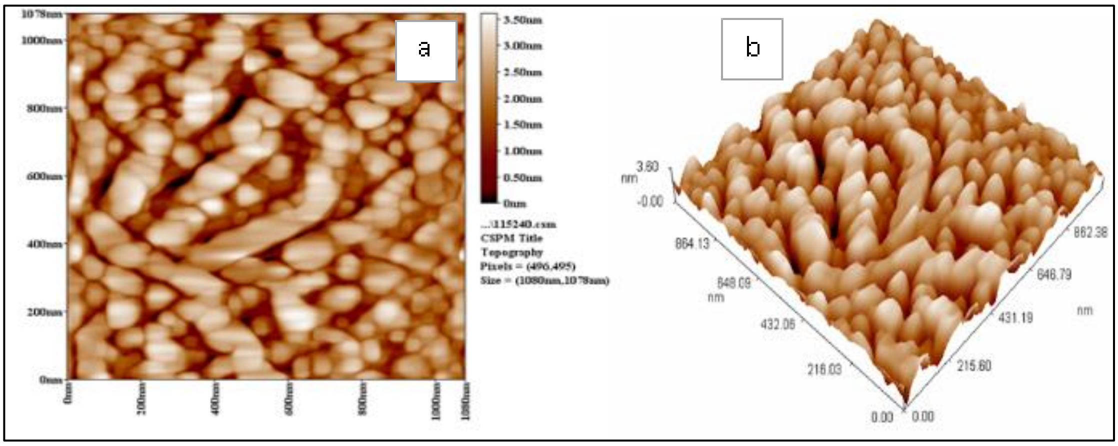


Figure 4: AFM Surface scan of anodized low carbon steel at annealed 900°C a. (2D) View, b. (3D) View.

Annealing is most frequently applied in order to soften carbon steel materials and refines its grains due to ferrite- pearlite microstructure [14, 15].

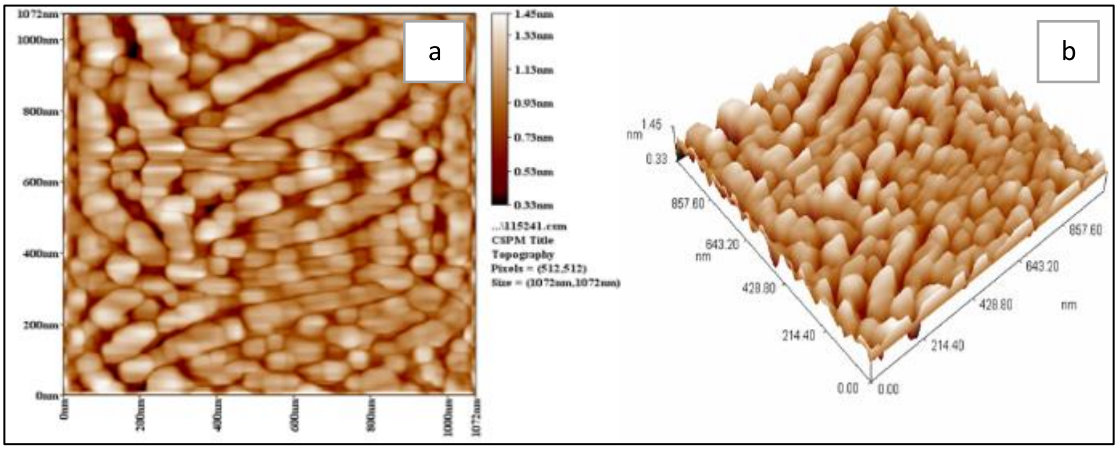


Figure 5: AFM Surface scan of anodized low carbon steel at annealed 1000°C
a. (2D) View, b. (3D) View

3-2 Polarization and Corrosion Rates Measurements

Polarization curve is commonly used as a plot of the electrode potential versus the logarithm of current density. Figures (6 & 7) indicates such curves, for low carbon steel without and with anodizing in 3.5 wt% NaCl solution ; which show that corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values are (-537 , -348) mV and (22.08 , 2.49)µA/cm^2) respectively

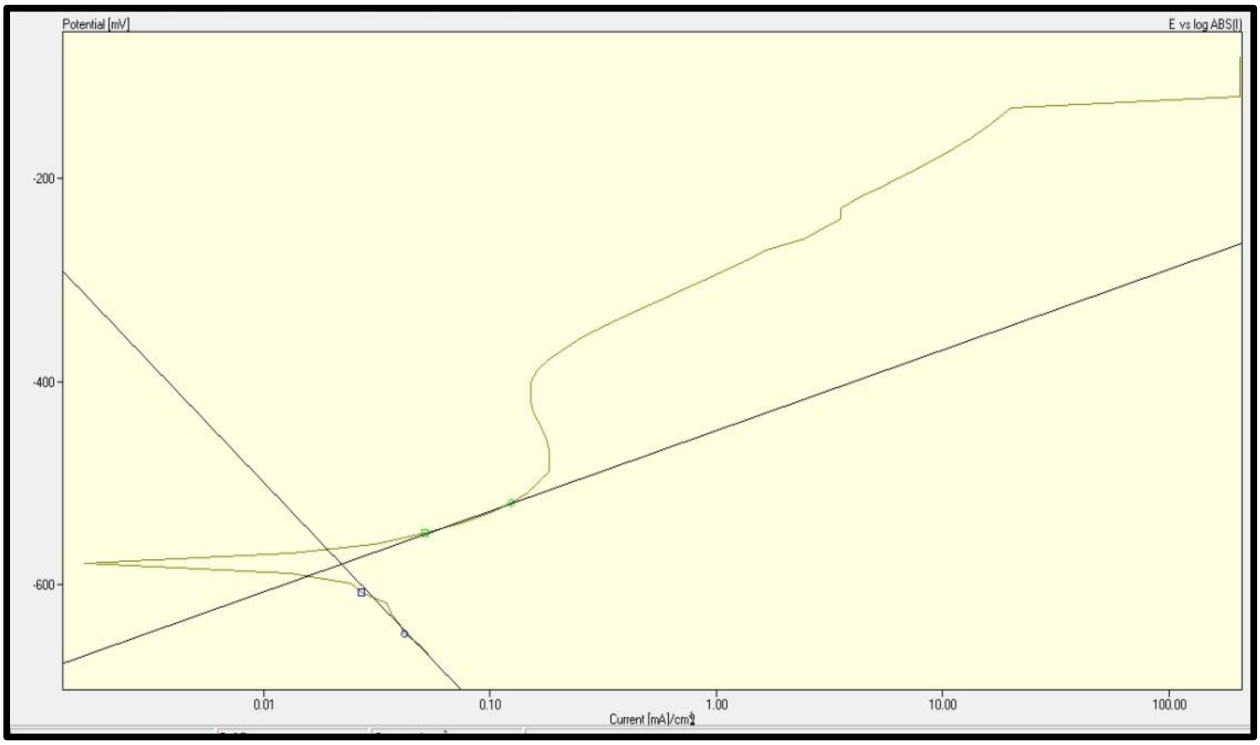
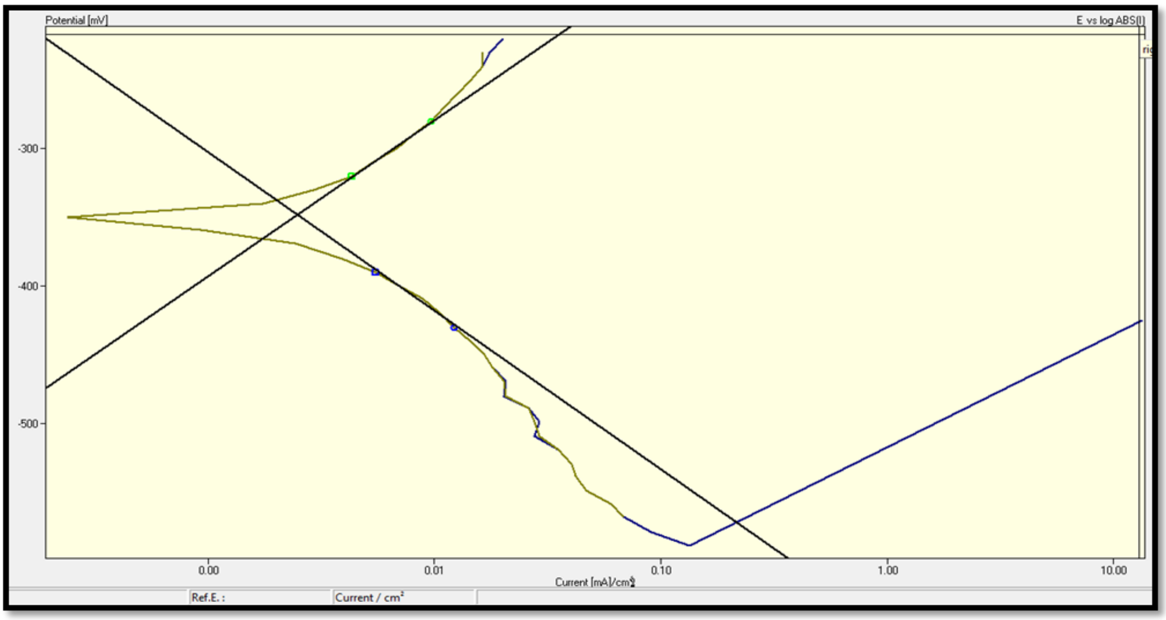


Figure 6: Potentiostatic polarization behavior of low carbon steel without anodizing

The potentiostatic polarization of anodized low carbon steel specimens are presented in Figures (8 to 10) which show cathodic and anodic polarization curves of anodized low carbon steel specimens in 3.5 NaCl wt % solutions , which show that corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of anodized anneal low carbon steel at 650 ,900,and 1000 °C values are (-336 mV, -274 mV, and -266 mV) and (2.12µA/cm^2, 1.17µA/cm^2,and1.06µA/cm^2) respectively



.**Figure 7:** Potentiostatic polarization behavior of anodizing low carbon steel without annealing

The corrosion rate measurements for as received, anodized without annealing, anodized annealed low carbon steel specimens are shown in table (2). The higher corrosion rate is observed for anodized annealed specimens at 1000°C due to higher film thickness and lower pore diameters as mention before

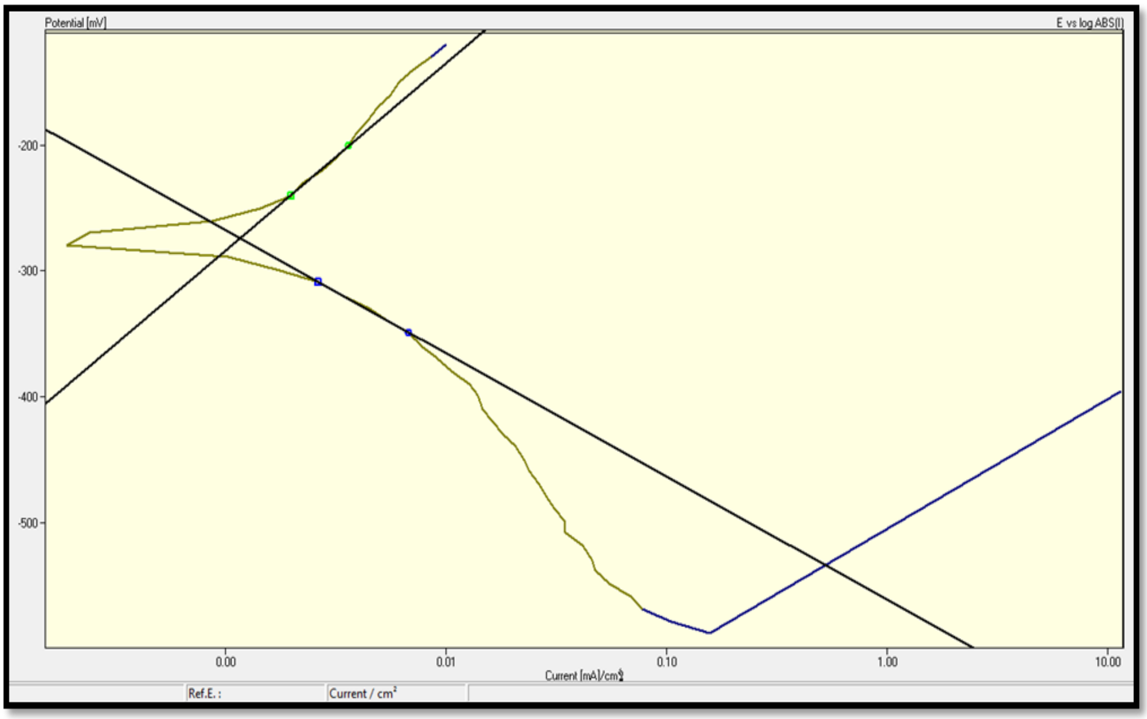


Figure 8: Potentiostatic polarization behavior of anodizing annealed low carbon steel at 650°C.

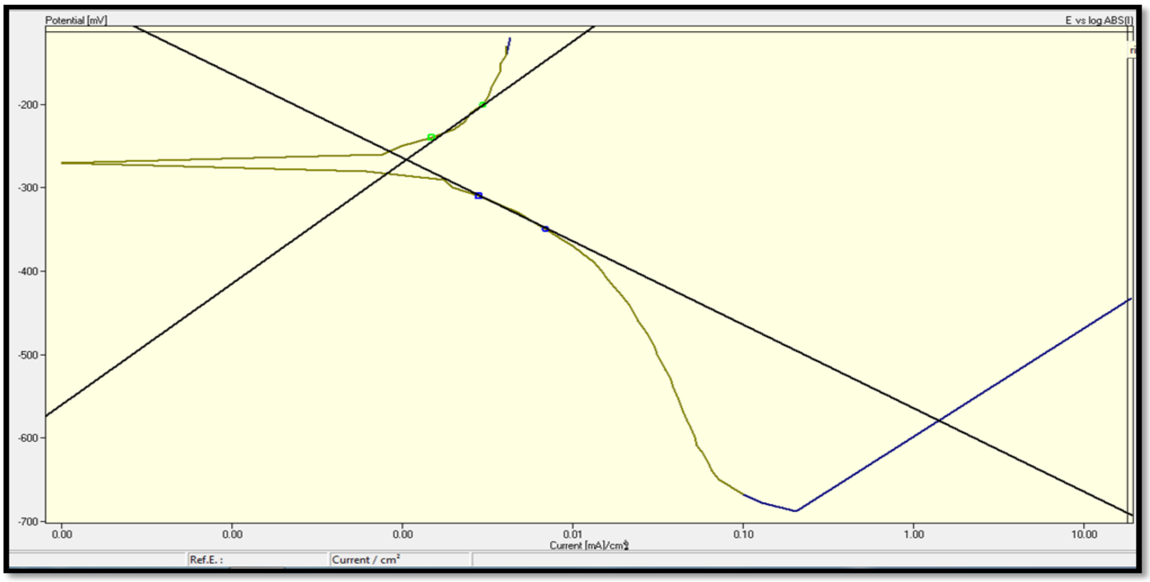


Figure 9: Potentiostatic polarization behavior of anodizing annealed low carbon steel at 900°C.

Table 2: corrosion rate of anodized low carbon steel at different treatments

Type of Treatment	$I_{corr.}$(μA/cm^2)	$E_{corr.}$ (mV)	Corrosion rate (mpy)
Low carbon steel without anodizing	22.08	-579.8	20.2141
Anodizing low carbon steel without annealing	2.49	-348.0	2.2795
Anodizing annealed low carbon steel at 650°C	2.12	-336.1	1.9408
Anodizing annealed low carbon steel at 900°C.	1.17	-274.1	1.0711
Anodizing annealed low carbon steel at 1000°C	1.06	-266.2	0.9704

These anodized films provide improved corrosion protection for steel and these are also suitable substrates for the bonding of organic coatings. The microstructural evolution of the material during the heat treatment processes played a fundamental role on the corrosion behavior of the material.

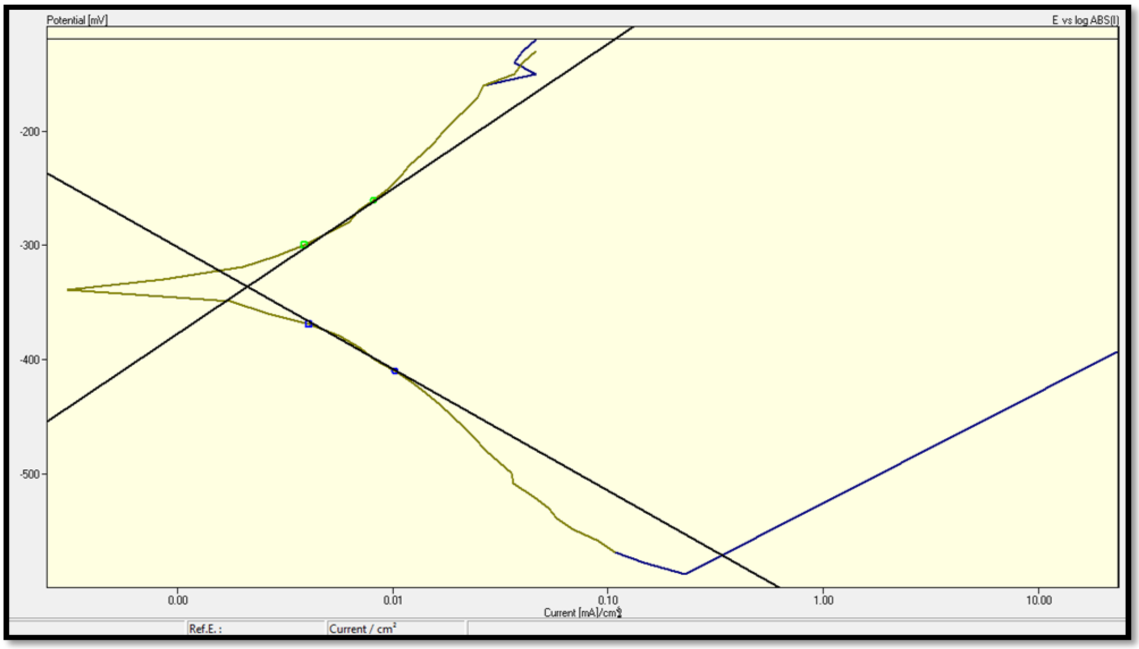


Figure 10: Potentiostatic polarization behavior of anodizing annealed low carbon steel at 1000°C.

The specimens after corrosion test were examined by optical micrographs. Figures 11 shows polarization specimens of low carbon steel and low carbon steel nanoparticles formed by anodizing process at 15 V with annealing at different temperatures (650, 900, and1000) °C for1 h, respectively. The above graphs show that anodized low carbon steel are more corrosion resistant than low carbon stee

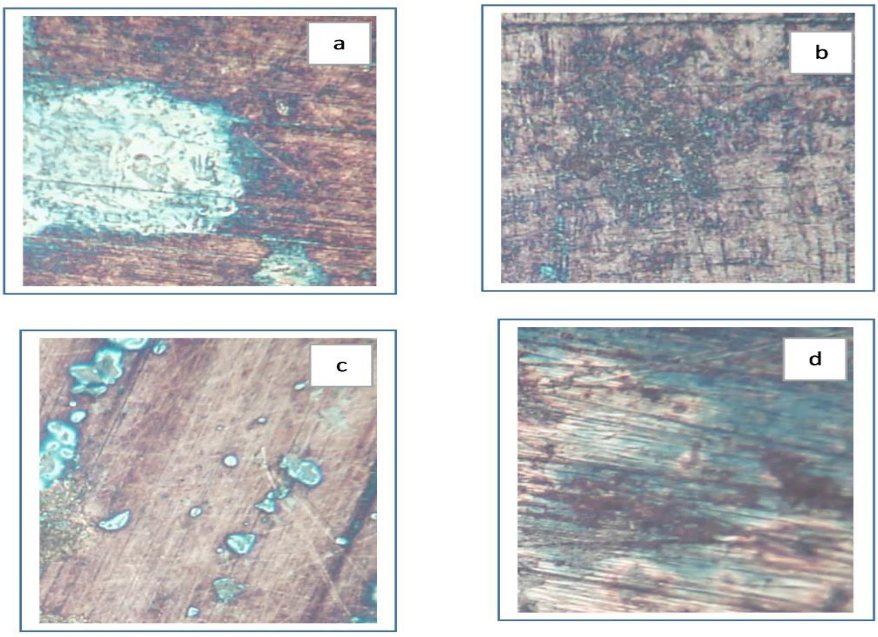


Figure 11: Optical micrographs showing the microstructures of anodized low carbon steel before and after heat treatment: (a) as-cast, (b) annealed at 650°C, (c) annealed at 900°C, (d) annealed at 1000°C.

From figure above shows black phases are cementite which appears as networks throughout the surface because of high temperature used for low carbon steels. The microstructure of the annealed steel is mostly spheroid zed cementite and ferrite. This periodization was the result of the relatively slow cooling undergone by the steels during the annealing treatment. , lamellar pearlite is quite resistant to wear as he found in making wear tests on cast iron that the main factor which governed the resistance to wear of cast iron was the percentage of pearlite. Evidently the presence of either free ferrite or free cementite (as spheroids) is detrimental to the wear resistance of normalized carbon steel. That free ferrite is distinctly harmful in low-carbon steels, all of which exhibited low resistance to wear [16].

4-Conclusion

The investigation of heat treatment effects on anodized low carbon steel has been experimentally studied and the following points were concluded from the study:

1- The annealing process is a heat treatment process used to improve anodizing behavior of low carbon steel due to stress relives.
2- The corrosion resistance of anodized low carbon steel is higher than non-anodized low carbon steel.
3- All annealing temperatures used in this work improve corrosion resistance of anodized low carbon steel.
4- The best conditions for higher corrosion resistance is anodized low carbon steel when annealed before anodized low carbon steel at 1000˚C.

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تأثير المعاملات الحرارية على مقاومة التآكل للصلب الكاربوني المنخفض المؤنود

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الجامعة التكنولوجية

الخلاصة :
يتضمن البحث دراسة تأثير المعاملات الحرارية لانودة الصلب الكربوني باستخدام القياسات الكهروكيميائية . أجريت معاملة حرارية للصلب الكربوني المنخفض قبل الانودة بالتلدين عند درجات الحرارة (1000,900,650) م° لمدة ساعة واحدة ثم انودة سطح الصلب الكربوني المنخفض غير الملدن والملدن بالدرجات الحرارية اعلاة في محلول هيدروكسيد الصوديوم . يتم دراسة السلوك الكهروكيميائي للصلب الكربوني المنخفض , الصلب الكربوني المنخفض بعد الانودة و الصلب الكربوني المنخفض الملدن بالدرجات الحرارية أعلاه المؤنود في (3.5 wt% NaCl) محلول كلوريد الصديوم بأستخدام المجهاد الساكن . معدلات التآكل للمواد أعلاه تم قياسها . تشير نتائج معدلات التأكل المقاسة الى تحسين في مقاومة التأكل للصلب الكربوني المنخفض الملدن بالدرجات الحرارية اعلاة بعد الانودة . تم فحص خصائص السطحية لطبقة الانودة باستخدام مجهر القوة الذرية (AFM) والمجهر الضوئي لفحص العينات قبل وبعد أختبار التآكل . تشير النتائج العملية بأن أفضل ظروف للحصول على أعلى مقاومة تأكل هو للصلب الكربوني المنخفض المؤنود عند التلدين عند درجة حرارة 1000م°.