

Effect of Different Coating Techniques with Aluminum on the Corrosion Behavior of Stainless Steel 316L in Seawater

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Abstract

This study involves effect of aluminum coating by using different techniques (Aluminizing, Flame spraying, and Hot dipping) on corrosion behavior of stainless steel 316L in seawater. Cathodic and anodic regions are studied by using potentiostat to measure the corrosion parameters through Tafel method which include open circuit potential (E_{ocp}), corrosion potential (E_{corr}), and corrosion current density (i_{corr}) in addition to calculation of coating corrosion rates (R).

The results indicate that the corrosion rate for coated specimens by aluminizing and flame spraying techniques were less than the values before coating but coating with hot dipping technique gives higher rate than the non coated samples, where the results take the following sequence:

Corrosion Rate ($\mu\text{m/y}$) *coating sample by using pack cementation aluminizing* < *coating sample using flame spray* < *coating sample using hot dipping*

The potentials with time were interpreted in order to study the evolution of the film chemistry as it came to equilibrium with solution where the results observed that the aluminum coating by aluminizing reaches to the steady – state faster than other samples. Also the galvanic current density with time were discussed where the results indicates, in general, the transients for specimens show an initial sharp decrease in galvanic current exhibited by all coated specimens followed by a more steady, but erratic decrease in the galvanic current.

Keywords: Aluminum coating. Stainless Steel 316L, Flame Spraying, Hot dipping, Aluminizing, polarization behavior of Aluminum coated-stainless steel.

1. Introduction

Aluminum is used as a protective coating for iron and steel and also for some high- and medium-strength aluminum alloys. In some situations the optimum protection is obtained by using an aluminum alloy as the protective coating [1]. Aluminum is applied also as a decorative coating on both metallic and non – metallic surfaces. Several methods of applying the aluminum coating are available, and the method selected depends to a large extent on whether the protective or decorative aspect is more important. Some methods of coating will be excluded by the geometry of article to be coated, while others will be excluded by the chemical or physical nature of the article.

Protective coatings are probably the most widely used products for corrosion control. They are used to provide long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials to preserve their

strength and integrity. The main function of a protective coating is to isolate structural reactive elements from environmental corrosives. The fact that protective coatings occupy only a very small fraction of the total volume of a system is quite telling of the heavy requirements imposed on these materials. A coating must provide a continuous barrier to a substrate, and any imperfection can become the focal point for degradation and corrosion of the substrate.

Aluminum coatings can be applied to steel by hot dipping, cementation, ion vapor deposition, and spraying. Ion vapor deposition is a relatively new process, and spraying is the only process that has been used extensively over a long period of time. Pack cementation is widely used for gas turbine components. In soft waters aluminum is cathodic with respect to steel; however, in seawater or some fresh waters containing chloride ions or sulfate ions, aluminum may become anodic to steel, and aluminum coatings should therefore corrode sacrificially and provide cathodic protection to

steel. However, as noted below, this may not always be the case [1].

Coating have three basic mechanisms for protecting metals from corrosion, although more than one of these mechanisms may be used by a coating. These mechanisms are:

Barrier Protection: Most coatings provide corrosion protection by forming a barrier relatively impermeable to moisture and electrolytes necessary for corrosion. Obviously, for optimum protection, the barrier should be as impermeable, thick, and continuous as practical.

Cathodic Protection of Steel: Some protective coatings have a high loading of fine zinc particles, so the particles in the cured film are in electrical contact with each other and with the underlying steel. This permits a type of cathodic protection. Presently, two basic types of zinc – rich coatings are used on steel: organic and inorganic products.

Inhibitive Pigments: Some pigments are added to primers to inhibit corrosion at the coating/metal interface. Red lead is the most common example of an inhibitive pigment [1].

There are many studies about coating of steel with different materials. Sun Hu-yuan and co-workers studied the electrochemical corrosion behavior of hot dip coating in artificial seawater [2]. While J. Creus and co-workers studied evaluation of protective coatings onto steel, through electrochemical techniques [3].

Corrosion performance of polypyrrole coating applied to low carbon steel by an electrochemical process was studied by Iude O. Iroh and Wencheng Su [4]. Krokmal'nyi studied electrochemical characteristics of corrosion in aluminum coatings in a chloride solution with corrosion fatigue [5].

S. Zein WI Abedin studied coating of mild steel by aluminum in the ionic liquid [1- ethyl- 3- methylimidazolium bis(tri fluoromethylsulfonyl) amide] ([EMIm]Tf₂N) and its corrosion performance [6].

Iqbal Hussain and co-workers studied the electrochemical performance of flame sprayed and high velocity oxy-fuel sprayed aluminum coatings in simulated splash zone service conditions [7]. While Maria and co-workers studied characterization of organic-inorganic hybrid coatings for corrosion protection of

galvanized steel and electroplating ZnFe steel [8]. S.T. Vagge and co-workers studied the effect of deformation on the electrochemical behavior of hot – dip galvanized steel sheets [9].

2. Experimental Part

2-1 Materials

The substrate material used for the investigation was a plate of stainless steel 316L. with a nominal composition {(C : 0.28), (Si : 0.92), (Mn : 1.92), (p: 0.041), (S: 0.027) , (Cr :18), (Mo: 2.55), (Ni :12.6), (Reminder Fe: (wt.%))} which is received from general company for heavy mechanical industry. Specimens were cut to dimensions of approximately {(20×20mm) for potentiostat inspection, (10×10mm) for coating thickness}, and then manually ground using SiC abrasive paper to a 600-grade finish. The experimental solution that used as corrosion environment was seawater 3.5% NaCl, all experiments were performed at room temperature.

2-2 Coating Techniques

The specimens were degreased before being coated by the selected techniques:

2-2-1 Pack Cementation

In aluminizing pack cementation technique aluminizing powder mixtures were prepared by weighing out and mixing appropriate amount of powders from Al in (20%), Al₂O₃ in (75%) (with tabular particle shape) which is received from Alcoa company and chloride salt (NaCl) in (5%). The average particle sizes of Al is (1000µm) and Al₂O₃ (850 µm). The selected amount of chloride salts (NaCl) which is, 5%, was assessed as possible activator percents for the intended pack aluminizing process at temperature 650 °C. This salt was manually ground with a mortar and pestle, but not sieved, before being weighed out and added into aluminizing powders. The in-pack process was used to pack aluminize the identified specimens. With this process, the substrates were buried in pack powders charged into a rectangular stainless steel retort (250 mm length and 15 mm width), which was then sealed with stainless steel lid and fire clay.

The fire clay seal was cured for at least 2 h at approximately 110 °C. The pack was then

loaded into an alumina muffle furnace, which was subsequently circulated with argon and the temperature was raised to and held at 150 °C for 2 h to facilitate further cure of the cement. The furnace temperature was then raised to a final coating temperature, normally at 650 °C, at a heating rate of 7 °C per minute and was held at this temperature for a required duration (4h). The furnace was then cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon gas flow.

2-2-2 Flame Spray

Flame spray coating is an overlay deposition process. In this study, the coating material is a powder of aluminum, is applied on the surface of the base material through a melting process. The feedstock material (powder) is heated by using a special heat source. In this process a powder, 850 µm in size, is injected with a carrier gas to the flame beam traversing on the surface of the material to be coated (stainless steel 316L in this study). The powder absorbs energy from the flame beam, starts heating and melting in flight, and deposits on the surface of the base material. Part of the energy is also absorbed by the surface causing controlled melting of a thin layer of the base material. This ensures formation of a real metallurgical bonding between the coating and the base material. A melt pool of the coating material is formed, which in turn results in coatings without porosity. The mixing between the two materials (coating and base material), i.e. spraying, must be as small as possible to utilize the properties of the coating material (60 sec in this study).

2-2-3- Hot Dipping (Hot dip coatings)

Coating materials in the form of solids are melted in a tank furnace, using the energy of gas burned in burners. Since coating materials are predominantly metals and the melting point of used coating material is (660°C), coating made from it is traditionally called hot dip. Properties of hot dip coating are decided by surface preparation, chemical composition of the metallic material (purity and composition of alloy) and its temperature, time of soaking of the objects in the bath (30sec in this study) and by the substrate

material. Before dipping into the bath, the object is degreased, The fluxes (most often mixtures of sodium chloride and ammonium chloride) may also be added to the bath{in this study sodium chloride has been used as fluxes}.

2-3 Corrosion Test

2-3-1 Electrochemical Measurements

Polarization experiments were performed on Potentiostat with electrochemical standard cell with provision for working electrode (SS 304), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an SCE reference electrode.

Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 0.5 mV/sec. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slopes.

2-4 Coating Thickness Measurements

The thickness of the aluminized layer was estimated from a fractured section of a test piece coated (pack cementated, thermal sprayed, hot dipped) along with the work. A cross section of the test piece is grinded and polished with grinding papers (220, 400, 600, 800, 1000, and 1200) then with diamond paste, etched with a corrosive aching solution (parcel) then washed with water and ethanol, dried and inspected under optical microscope, its image is projected on to the screen of a camera of optical microscope at known magnification rule.

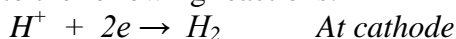
Fig.(1) show the coating thickness values for each selected coating techniques of stainless steel 316L coating systems.

3- Results and Discussion

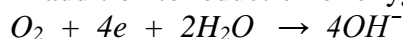
3-1 Potentiodynamic Polarization

Figs. (2) to (5) show polarization curves for the stainless steel before and after aluminum coating by using three different techniques. All polarization scans were obtained with the aid of 'Autotafel' software at scan rate of 0.5 mV/sec using a saturated calomel reference electrode. The different shapes of polarization curve for experimental samples shows the variation in surface activity with corrosive environment. The uncoated stainless steel sample can reacts with corrosive

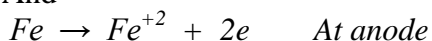
medium and undergo the corrosion according to the following reactions:



In addition to reduction of oxygen.



And



After aluminum coating, the corrosion potential shift in the positive direction by using pack cementation aluminizing and flame spray techniques. This would indicate a slight improvement of the corrosion protection properties. While the reverse behavior was observed by using hot dipping technique as shown in Table (1). Also using aluminum coating by aluminizing and flame spray technique decrease the corrosion current density, but it is increased by using hot dipping technique.

However, the decrease in current density and the shift of the corrosion potential in the positive direction is most likely to be attributed to the coating becoming less active in the sense that the pore in the coating are becoming blocked by aluminum corrosion product, effectively shielding the steel substrate and perhaps the coating from the corrosive electrolyte [10,11].

Initially, the freshly applied coatings are expected to exhibit a large number of open pores, resulting in the direct exposure of the substrate to the corrosive electrolyte and therefore the subsequent rapid corrosion of the adjacent aluminum coating through galvanic interaction. This will result in the localize development of insoluble aluminum corrosion product (aluminum oxides), which will settle in the pores thus blocking the exposure of the steel substrate to the corrosive electrolyte [10, 11, 12, 13].

Ultimately, this process will prevent the flow of ions to the steel substrate, eliminating the driving force for galvanic corrosion.

3-2 Potential Measurements

Figs. (6) to (9) show the variation of open circuit potential (E_{ocp}) with time for all experimental specimens before and after aluminum coating. The potential of the sample was followed as a function of time in order to study the evolution of the film chemistry as it came to equilibrium with solution.

The values of E_{ocp} were recorded after same time for all experimental solutions as listed in Table (1). The aluminum coating by using aluminizing pack cementation technique shift the (E_{ocp}) to more noble value, which indicates the film chemistry changes as the potential approaches the steady – state value. While the coating with hot dipping and flame spray technique, shift the (E_{ocp}) to value that is more active compared with the value for stainless steel before aluminum coating.

From shape of the relationship between the potential and time, it is significant that the aluminum coating by aluminizing reaches to the steady–state faster than other samples followed by the Al-coating with flame spray and then the sample before coating. Finally, the coated specimen with hot dipping technique has some noise and needs more time so that reaches to the steady–state.

3-3 Galvanic Current Measurements

Figs. (10) to (13) show the variation with time of the galvanic current before and after Al-coating on stainless steel. Generally, the transients for specimens show an initial sharp decrease in galvanic current exhibited by all coated specimens followed by a more steady, but erratic decrease in the galvanic current. The decrease in galvanic current exhibited by the coated specimens throughout the exposure period is likely to be attributed to the steady built–up of aluminum corrosion product on the surfaces of the coated specimens as a result of the corrosion of the coated surface.

These variations in the galvanic current flow may possibly be explained by the vigorous nature of testing in that the development of surface scales (aluminum corrosion product) on the surfaces of the coated specimens may have gone through cycles of forming, dislodging and re – forming, thus resulting in the variations of current flow between the aluminum coatings (anode) and the separate stainless steel electrodes (cathode).

3-4 Coating Corrosion Rates

The corrosion rates for the coated specimens may be determined from the linear polarization measurements. However, as linear polarization measurements were obtained under coatings conditions, a more realistic

approach would be to use the measured galvanic current and thus determine the corrosion rates through Faraday calculations as given by equation below [14].

$$\text{Corrosion Rate}(\mu\text{m}/\text{y}) = K \cdot \frac{ai}{nD}$$

Where (K) is a constant (3.27), (a) is the atomic weight of aluminum in grams, (i) is the current density in $\mu\text{A}/\text{cm}^2$, (n) is the number of electrons lost – valence change for aluminum, and (D) is the density of aluminum in g/cm^3 .

The results of corrosion rate of specimens listed in Table (1) which takes the following sequence of decreasing the rate:

Coating Corrosion Rate ($\mu\text{m}/\text{y}$)

pack < flame < hot
cementation spray dipping
aluminizing

4- Conclusion

During the corrosion protection by using aluminum coating with different techniques, it is shown that the Al-coatings with pack cementation aluminizing gives good results – corrosion resistance – compared with the Al-coating by flame spray and hot dipping techniques.

Table (1)

Corrosion parameters of stainless steel before and after aluminum coating by using different techniques at room temperature in seawater.

Samples	Open Circuit potential $-E_{ocp}(\text{mV})$	Corrosion potential $-E_{corr}(\text{mV})$	Corrosion current density $i_{corr}(\mu\text{A}.\text{cm}^{-2})$	Coating corrosion rate $\times 10^{+3}(\mu\text{m}/\text{y})$
Before coating	262	1090.5	381.47	-
After coating by using aluminizing	179	992.2	331.20	3.610
After coating by using flame spray	477	1003.4	340.08	3.707
After coating by using hot dipping	655	1242.5	649.85	7.083

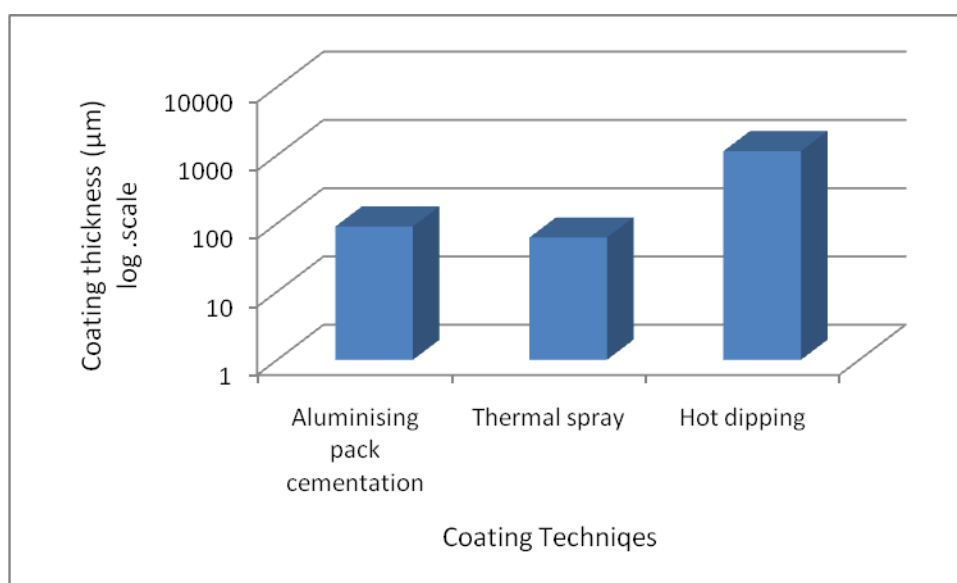


Fig. (1) Show the coating thickness values for each selected coating techniques of stainless steel 316L coating systems.

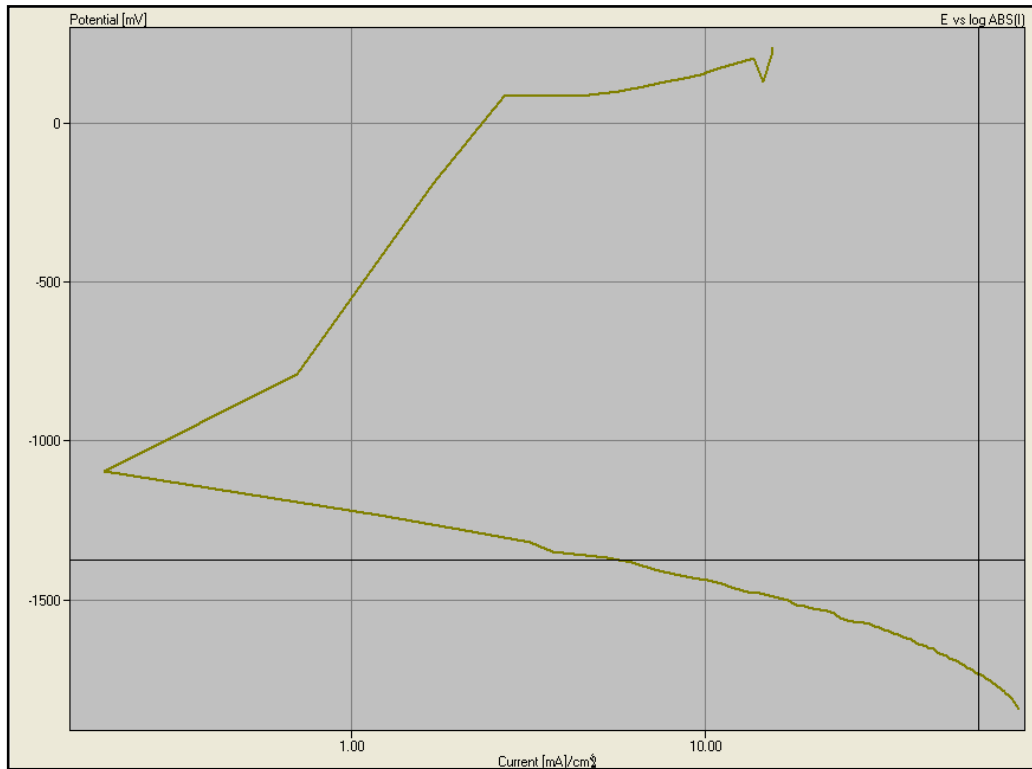


Fig. (2) Polarization curve of stainless steel before coating at room temperature in seawater.

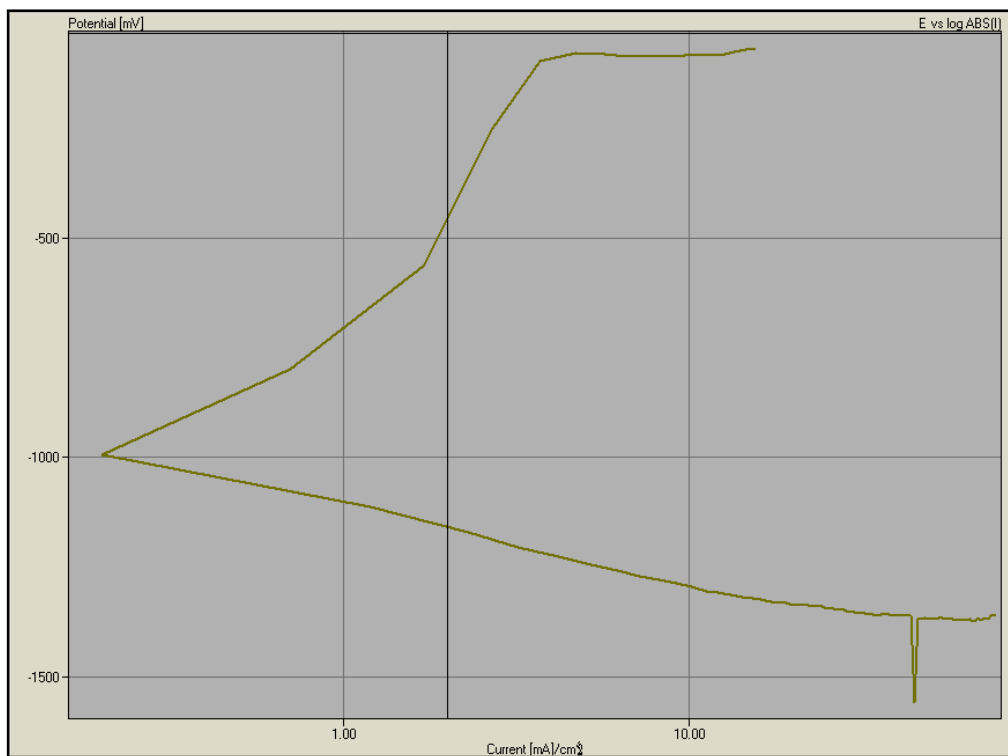


Fig. (3) Polarization curve of stainless steel after aluminum coating by using pack cementation aluminizing technique at room temperature in seawater.

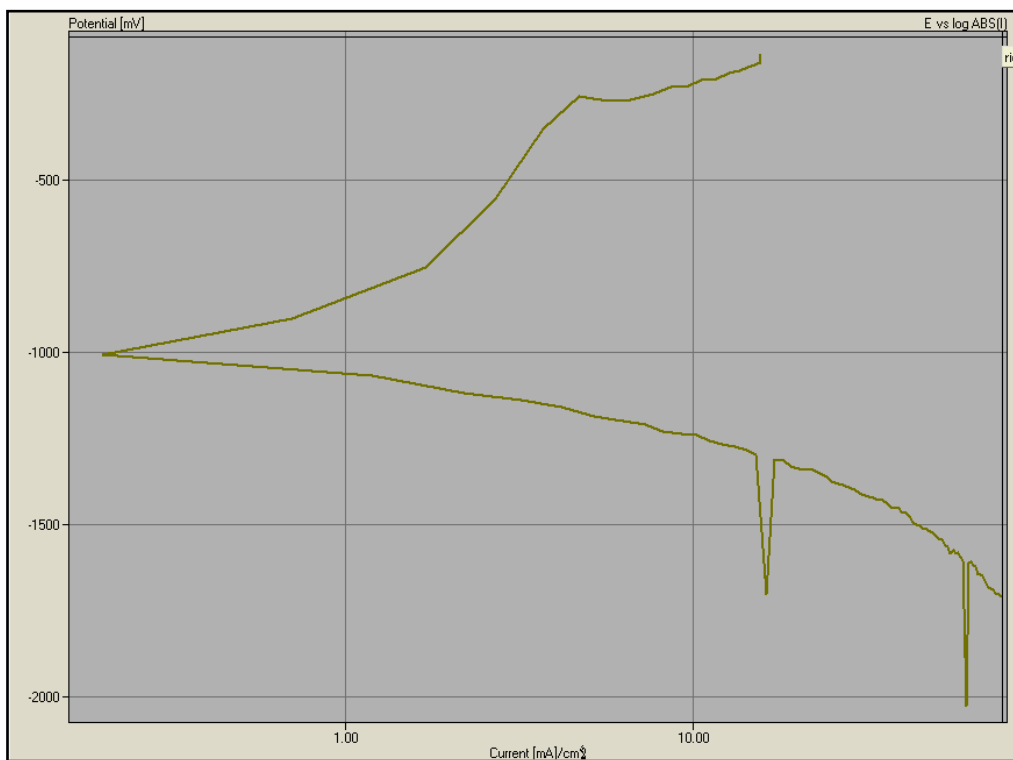


Fig. (4) Polarization curve of stainless steel after aluminum coating by using flame spray technique at room temperature in seawater.

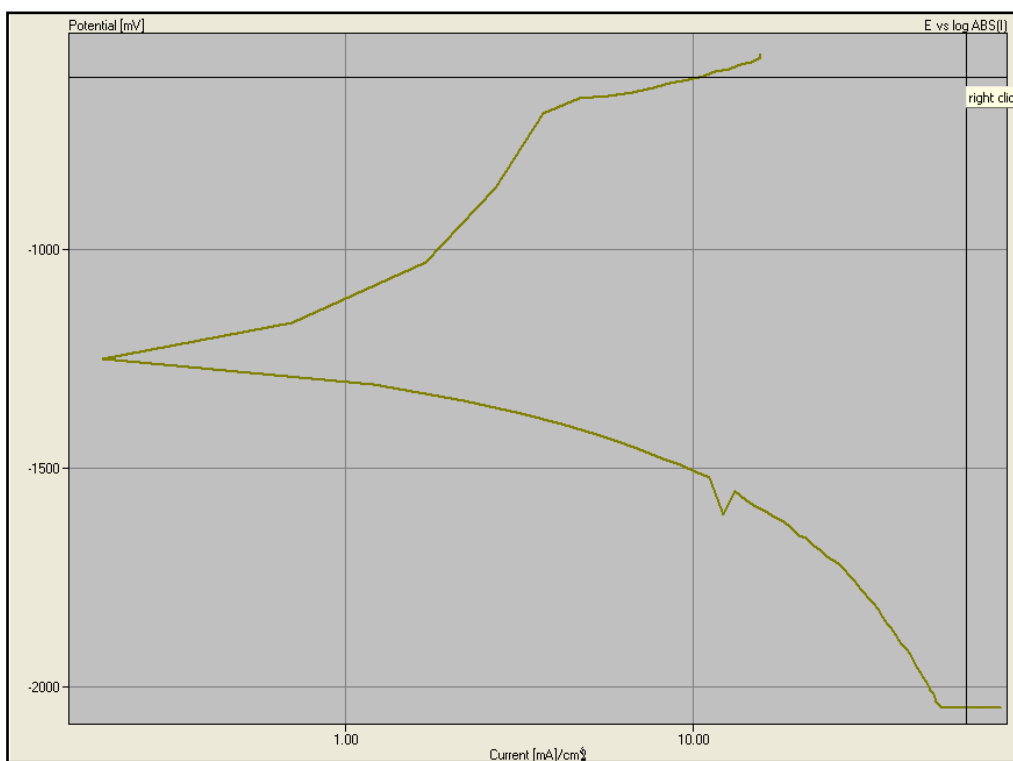


Fig. (5) Polarization curve of stainless steel after aluminum coating by using hot dipping technique at room temperature in seawater.

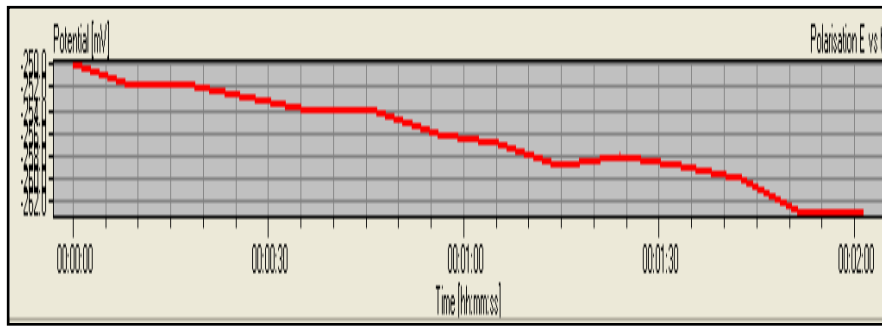


Fig. (6) The variation of potential (mV) versus time (sec.) plot for stainless steel in 3.5%M NaCl solution before aluminum coating at room temperature.

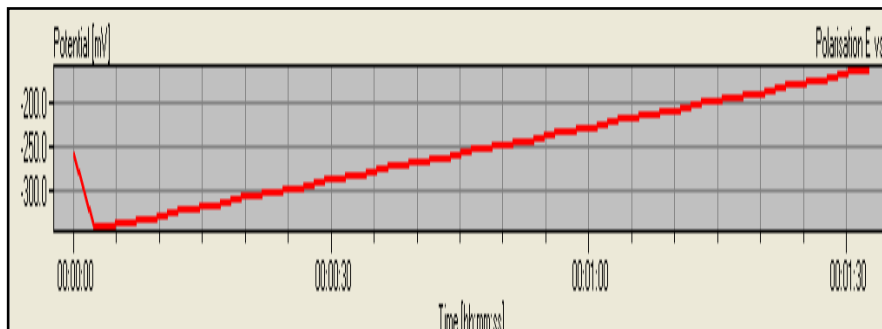


Fig. (7) The variation of potential (mV) versus time (sec.) plot for stainless steel in 3.5%M NaCl solution after pack cementation aluminizing at room temperature.

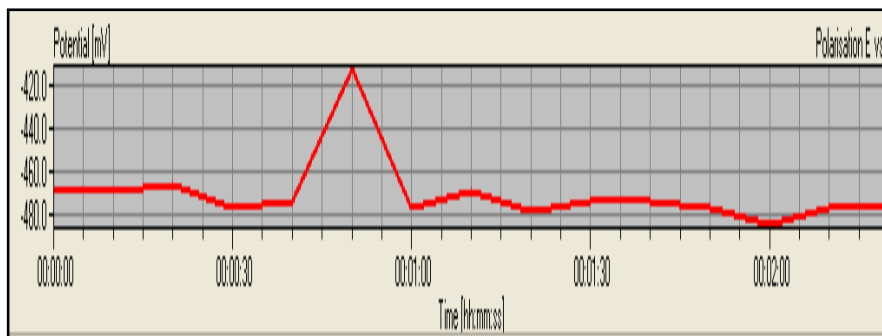


Fig. (8) The variation of potential (mV) versus time (sec.) plot for, stainless steel in 3.5%M NaCl solution after flame spray at room temperature.

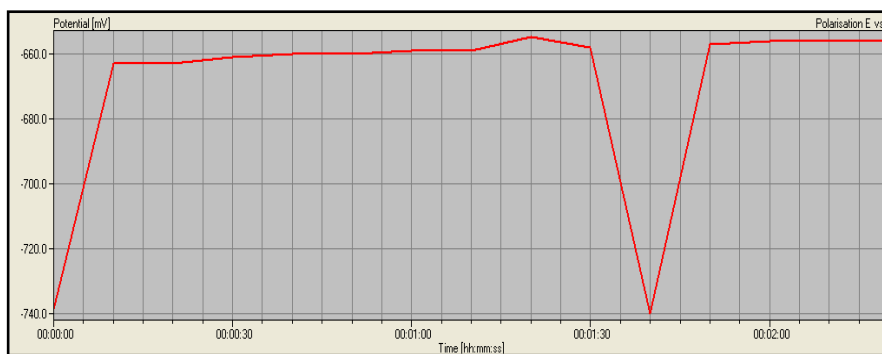


Fig. (9) The variation of potential (mV) versus time (sec.) plot for, stainless steel in 3.5%M NaCl solution after hot dipping at room temperature.

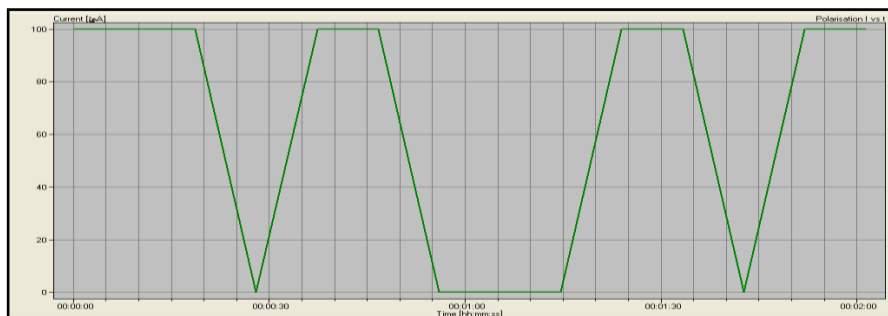


Fig. (10) The variation of current density (μA) versus time (sec.) plot for stainless steel in 3.5%M NaCl solution before aluminum coating at room temperature.

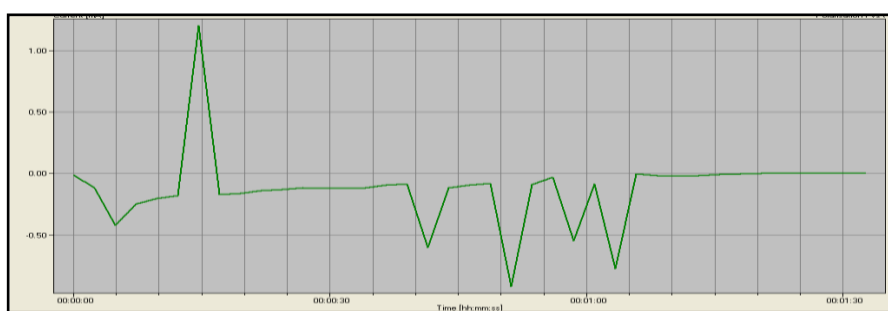


Fig. (11) The variation of current density (μA) versus time (sec.) plot for Stainless Steel in 3.5%M NaCl solution after aluminizing at room temperature.

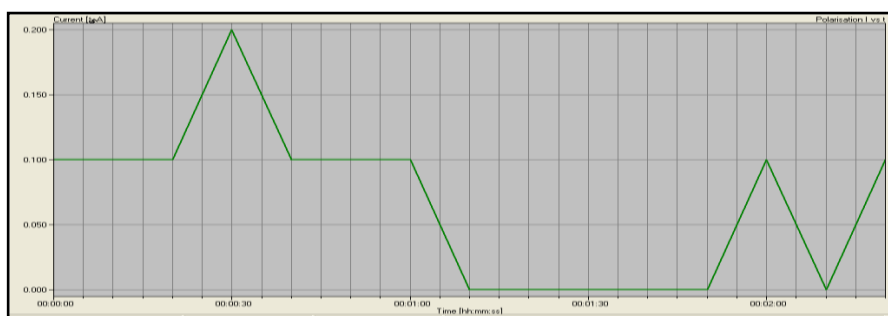


Fig. (12) The variation of current density (μA) versus time (sec.) plot for stainless steel in 3.5%M NaCl solution after flame spray at room temperature.

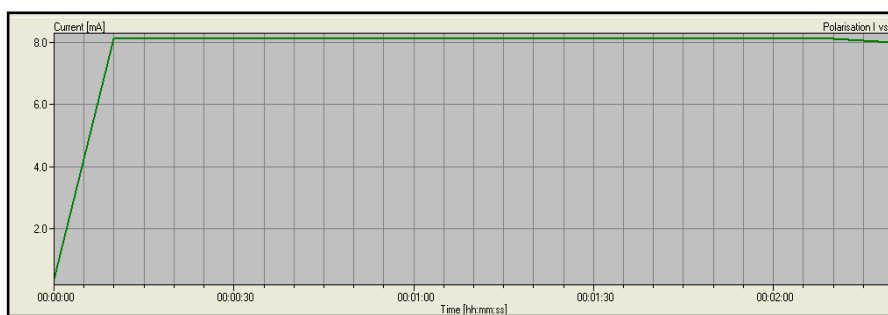


Fig. (13) The variation of current density (μA) versus time (sec.) plot for stainless steel in 3.5%M NaCl solution after hot dipping at room temperature.

5- References

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الخلاصة

أن هذه الدراسة تضمنت أثر الطلاء بالألمنيوم باستخدام تقنيات مختلفة (الامنة، الرش الحراري، التغطية الساخن) على تصرف التآكل لسبيكة الفولاذ المقاوم للصدأ 316L. تم دراسة المناطق الكاثودية والانودية باستخدام المجهاد الساكن لقياس متغيرات التآكل بطريقة تافل، والتي تضمنت جهد الدائرة المفتوحة (E_{oc})، جهد التآكل (E_{corr}) وكثافة تيار التآكل (i_{corr}) إضافة إلى حسابات معدلات تآكل الطلاء (R). وأوضحت النتائج أن معدل التآكل للعينات المطلية بتقنيات الامنة والرش الحراري حقق قيمة أقل من قيمه قبل الطلاء (للعينات غير المطلية)، ولكن الطلاء بتقنية التغطية الساخن أعطت معدل أعلى حيث ان تسلسل حساب معدل تآكل الطلاء كان كما يلي:

معدل التآكل (مايكرومتر/سنة)

الطلاء باستخدام > الطلاء باستخدام > الطلاء باستخدام
تقنية الالمنة الرش الحراري التغطيس الساخن

لقد تم تفسير علاقة الجهود مع الزمن وذلك لدراسة الطبقة المتكونة على السطح في حالة التوازن مع المحلول وقد بينت النتائج ان السطوح المطلية بتقنية الالمنة تصل الى مرحلة التوازن اسرع من النماذج الاخرى المطلية بتقنياتي الرش الحراري والتغطيس الساخن. كما تم دراسة العلاقة بين كثافة التيار مع الزمن واطهرت النتائج عموماً حصول نقصان حاد في التيار يعقبه الوصول الى مرحلة التوازن مع حدوث نقصان شاذ في قيمة التيار ولجميع العينات المطلية.