Eng. & Technology, Vol.24, No.3, 2005

Improvement of Corrosion Resistance for Carbon Steel Alloy (ST-52) used in Marine Environments

Dr. Sami A. Ajeel[1], Jamal Ibrahim Hussein[2] & Talib Mohamed[3]

Received on: 1/11/2004
Accepted on: 18/4/2005

Abstract

Carbon steel alloy types (ST-52-3RR) are widely used in constructing marine environments and other engineering structural applications due to their good corrosion resistance, mechanical and physical properties. It suffers from corrosion specially in sea water.

In order to improve the alloy properties and to protect it from corrosion, the alloys must be protected in many methods. In this study, surface coating technology used to provide one of the possibilities of control corrosion and to improve material properties. The surface coatings are applied by thermal spray coating method to improve the corrosion resistance of alloys (ST-52 -3 RR).

Thermal spray coating is used due to its high reliability, ease in application and operation, its availability and availability of the material used in coating.

Electrochemical techniques including potentionstatic measurements are used together with immersion tests in 3.5% NaCl to evaluate the performance of the steel (ST-52-3RR) in marine environment.

This study indicates the beneficial of the Aluminum powder spray coating sealed by epoxy coating on aluminum coating layer due to the reduction in corrosion rate. This reduction was noticed in weight loss method and low corrosion current density during polarization measurements.

(1) University of Technology
(2) Metallurgical & Production Eng. Dept,, University of Technology
(3) Chemical Eng. Dept,, University of Technology

تحسين مقاومة التآكل للفولاذ الكاربوني(ST-52) المستخدم في الأوساط البحرية

الخلاصة

يستخدم الصلب الكربوني نـــوع (ST-52-3RR) بشـــكل واســـع فـــي البنـــاء للتطبيقات بالأوساط البحرية والهياكل الهندسية الأخرى نتيجة لمقاومته العاليـــة

https://doi.org/10.30684/etj.24.3A.10
2412-0758/University of Technology-Iraq, Baghdad, Iraq

للتآكل وخواصه الميكانيكية والفيزياوية الجيدة حيث تعاني هذه التطبيقات من التآكل وخصوصا في ماء البحر.
هناك العديد من طرق الحماية والوقاية تستخدم لغرض تحسين خواص هذه السبيكة ووقايتها من التآكل . استخدمت تقنية الطلاء السطحي في هذه الدراسة كأحد الطرق للسيطرة على التآكل وتحسين خواص المواد . نفذت التغطيات السطحية بطريقة الرش الحراري لتحسين خواص التآكل للسبيكة (ST-52-3RR). استخدمت هذه الطريقة نتيجة لوثوقيتها العالية ، سهولة التطبيق والعمل ووفرتها وتوفر المادة المستخدمة في الطلاء.
تضمنت الدراسة قياس التآكل بتقنيات الكهروكيمياوية باستخدام جهاز المجهاد الساكن واختبار الغمر في محلول (3.5%) كلوريد الصوديوم لتحديد سلوك أو أداء الصلب (ST-52-3RR) في الأوساط البحرية .
تشير الدراسة إلى فائدة استخدام طريقة التغطية بالرش بمادة مسحوق الألمنيوم ثم تختم طبقة الألمنيوم بمادة الايبوكسي التي أدت إلى تناقص في معدل التآكل . لوحظ هذا التناقص في معدل التآكل بطريقة الفقدان بالوزن وكذلك بالانخفاض في كثافة تيار التآكل في قياسات الاستقطاب .

1. INTRODUCTION

Many metals suffer from corrosion, carbon steel alloys are one of them. Carbon steel alloys are extensively employed as structural components in the industrial practice, and some surface treatments like anodizing , chromating, painting, coating and cathodic production are used to improve their corrosion resistance .However, no substantial improvement was obtained in the most severe conditions, various physical deposition methods together with implantation techniques are used in order to obtain modified surfaces or coatings which in turn improve the corrosion (e.g. pitting), oxidation and wear resistance. The use of such techniques to increase the carbon steel resistance in the case of Cl^- ions attack was shown to be helpful [1].

The overall corrosion behavior of the coated steel depends not only on the electrochemical properties of the metallic coating. In tested saline solution, Al coating will protect low alloy steel because of its sacrifical behavior. Nevertheless, galvanic corrosion between coating and substrate is actually disastrous for aluminum. A thin deposit of titanium before the deposition of aluminum will reduce the dissolution of Al coating and enhance the overall corrosion behavior [2].

The use of metal sprayed coating systems began in 1977 when initial tests were carried out on steam values. It quickly became apparent that metal sprayed coating systems were providing long protection to the steam values and significantly reducing preservation maintenance man hours. The success of these original applications has spawned many more applications on structures and equipment in corrosion-prone areas.

Zinc and aluminum are the main metals which are spray coated because of their importance in galvanic protection [3]. Of the many surface-modification techniques to offer the most advantages, it is adaptable to a wide range of requirements, relatively inexpensive, easily controlled and therefore capable of producing repeatable results.

Coatings of aluminum are frequently used in marine environments. The U.S Navey uses aluminum coatings for corrosion protection of many ship components, because these materials are anodic to steel [4].

The electrochemical tests for galvanized and Zn- 55AL – Si coated steel showed that all these coatings provide cathodic protection to the substrate metal, the galvanic potentials are equal to-1050mV, – 1025mV and -55mV AL-Si coating respectively. It is believed that the superior performance of the Zn-25 Al alloy coating is due to its optimal combination of the uniform corrosion resistance and pitting corrosion resistance [5].

The aim of this work is to high light the corrosion behavior of Carbon steel alloys(ST-52) bared and Aluminum coated assisted epoxy in conditions resembling those encountered in marine environment using conventional and potenstiostatic techniques on term of electrochemical polarization and microstructure observations.

2. EXPERIMENTAL WORK

Potentiostatic polarization technique was used to investigate the corrosion behavior of carbon steel and coated with Aluminum in sea water solution which is considerable of 3.5% NaCl [6].

2.1 Materials

2.1.1 Substrate

The materials used are carbon steel (ST-52-3-RR).The chemical composition is shown in table (1) which is done in the specialized Institute of Engineering Industries and compared with the composition of the DIN* standard.

2.1.2 Metal Coating

Metal coating used to the substrate in this study was Aluminum powder supplied by BDH chemicals pool England.

2.1.3 Epoxy

In this study, selection of the best polymer for sealing the coating layer (Aluminum) , is called polyamid which consists of two type , the first hardener is Epikote 828 and resin 114 was used [7]. It consists of hardener and light resin with mixing ratio of [2:1] (i.e. two volume of light resin and one volume of hardener) .The second type of polymers contains [EP10] hardener and the same previous resin with ratio [3:1] . These two types are applied to the specimen and examined them to define the best type. The second type was better due to good adhesion with coating and closed the coating porosities. Table (2) shows the specification of epoxy.

2.1.4 Solution

3.5% NaCl water was prepared from analar NaCl and distilled water to simulate seawater.

2.2 Equipments and apparatus

1. Electrical Furnace:

The furnace used in heat treatment is Derotor type with the following specification: Multithermss-1100 °C, Frequency 50 HZ, Power 1600 watt, Voltage 220 volt and thermocouple type K.

2. Coating Thickness Measurement Device:

The (SEIDNER) model 7940 RIEDIN GENW GERM is used for coating thickness measurement.

3. Ultrasonic Cleaner:

The cleaner is Bandelin electronic , Berlin 45 (west made in W. Germany) . It is of type +Nr 1652/ 18068 , voltage 220 V , 0.5 A , Hf –leist 807 /60 , FTZ-Nr , C-924/72.

4. Digital Blance:

The Blance type Scaltec is used with SB A41 max 410 , d=0.0001 gm, management system , certified according to ISO 9001 , Germany.

5. Potentiostatic:

The potentiostatic used was supplied by SOLEA TACCASEL.

6. Chart Recorder:

The recorder used is of type TILOG- 101-EPL-2 , seriet B2 NO. 51951, Range 125 nA–125 mA, which made in France.

7. Voltmeter:

This is of the type [PRT10 - 0.5L] made in France.

8. Ameter:

This is of the type [MVN79] made in France.

2.3 Electrode Preparation

The working electrodes were prepared by cutting the alloys into specimens of (2 cm * 1 cm * 0.5 cm) .The specimens were annealed at 600 °C on derotor type furnace to release stresses [7]. Then, the samples were moulded in epoxy resin such that an area of 2 cm^2 was exposed to corrosion media. The moulded samples were successively polished using silicon carbide grit of 100, 200, 400, 600, 800 and 1000 grit size and final polishing was done using diamond paste in order to obtain a scratch free mirror finish .

The electrodes were ultrasonically cleaned with soap solution , degreased using acetone and thoroughly rinsed in distilled water and dried .

An identical procedure was followed for all the electrodes to avoid any experimental error.

2.4 The Procedure of Thermal Spray

Before thermal spray process, the substrate treatment with heat is useful to get homogenous and good adhesion as shown in (Figure 1).

The thermal spray method used to coat the carbon steel (ST-52), consists of two cylinders supplied by gauge, one for oxygen and the other for acetylene conjection with compressor to push the gas flow rate ratio to be [5:1]respectively. The pressure gas mixing 5 MPa. The gases mixed with another and flame in spray gun, the distance between the spray gun and substrate about 20 Cm and the angle of spray gun to spray is 90° [9]. The (SEIDNER) was used to measure the thickness of coating, the coating thickness is about 0.03mm, and the thickness of Aluminum coated with epoxy is about 0.04mm (The epoxy layer is about 0.01) .Specimens were given cleaning in an ultrasonic bath for 25 minutes dried, stored for further experimental steps.

2.5 Corrosion Rate Measurement:

Two methods were used for assessment and evaluation of the corrosion resistance of (St-52) ; immersion test and electrochemical methods as follow :

2.5.1 Immersion Test Method

Specimens of (1 x 2 x 0.5 cm) in dimensions were used . These specimens were abraded with different grades of emery paper by using 220 , 320 , 400 , 600 , 800 and 1000 grades successfully. After being washed with running tap water followed by distilled water , dried , degreased by washing them in acetone , dried with a clean tissue and they kept in adesicator over silica gel bed until the time to use .

For the weight loss measurements , the carbon steel alloy and carbon steel alloy coating with 0.03mm Aluminum, coating with aluminum and epoxy were completely immersed in 100 cm^3 of 3.5% wt NaCl solution at 25 °C in a conical flask [10] . They were exposed for periods of 5,10 , 15 and 20 days to corrosion media, then the weight loss was determined. This selection of immersion times because there is no weight loss appeared during a period of less than 5 days.

2.5.2 Open Cicuit Measurement

The free corrosion potentials for all tested were determined by recording the potential of the specimen with respect to SCE with time using the digital voltmeter. $E_{corr.}$ value was automatically recorded with variable value, till it reaches a steady state value. This steady state value can be considered the actual $E_{corr.}$ in this environment.

2.5.3 Potentiostatic Polarization Method

Polarization was carried out using potentiostatic. The potentiostatic was connected to voltmeter and a meter to read the current density.

The constant potential can be applied by the potentiostatic, while the change in current density when using the preselected potential, can be recorded automatically with time using the same recorder and the same circuit diagrams as shown in figure (2) which show electrical connection circuit diagram.

Carbon steel specimens uncoated and coated with aluminum are polarized at the applied potentials in the cathodic and anodic regions. The applied potentials are selected with the help of corrosion potential obtained in open circuit test and with sweep rat was 20 mV/min.

3. Results and Discussion

The corrosion behavior of carbon steel alloy (ST-52) and carbon steel coated with aluminum in 3.5% NaCl solution at 25°C have been investigated by weight loss and polarization techniques to determine the corrosion behavior of coated layer that has been obtained.

3.1 Weight Loss Measurements:

Table (3) summarizes 4 runs of corrosion rate (mdd) of carbon steel alloy and carbon steel alloy coated with Aluminum at 25 °C. Experiments were made in stationary solution at different times of immersion (i.e. 5-20 days). The corrosion rates are applied using the following relation.

$$\text{Corrosion rate } (mg / dm^2 .day) = \frac{\Delta w \left(\text{chang ein weight}\right)}{\text{surface area } (dcm^2) \times \text{time } (day)} \quad (1)$$

The results obtained as corrosion rate (mdd) versus time are shown in figures (3)and (4) .Figure (3) shows that the corrosion rate of uncoated specimens generally is time independent during the periods up to 15 days , then the corrosion rate decreases with time . The decrease in corrosion rate in the later time can be attributed to the appearance of the deposition on the surface which is removed during washing the specimens.

Figure (4) indicates that the corrosion rate of coated specimen with aluminum only decreases initially then after 10 days is time independent.

Figure (5) illustrates the general microstructure of carbon steel alloy specimen after immersion test which is similar to the microstructure of the specimen without immersion. This indicates that the exposed specimen surface did not show any corrosion morphologies which may be due to uniform corrosion and also removed corrosion depositions during washing the specimens.

Figure (6) shows optical micrograph for surface morphology of coated specimens with aluminum. This figure indicates surface defects such as roughness, deposited droplets during thermal spray process and mainly porosity, cracks and scratches.

The aluminum coated specimens are also sealed by epoxy which don't show any losses of weight. This indicates that epoxy resins closed any porosity and also prevent aluminum contact with sea water.

The corrosion rate measurements (Table 3) reveal lower corrosion rate values for carbon steel coated with aluminum compared with uncoated specimens. This indicates an improvement in corrosion resistance due to coating with aluminum . Figure (7) shows the efficiency improvements in corrosion rate due to coating with aluminum which is defined from the following relation :

$$\text{Efficieany \% in Corrosion Rate} = \frac{\text{C.R(Uncoated) C.R(Coated)}}{\text{C.R (Uncoated)}} \times$$

3.2 Potentiostatic Polarization Measurements:

3.2.1 Open Circuit Potential Measurements:

The variation of the open circuit potential (OCP) of carbon steel alloy (St-52-3RR) with time of immersion in 3.5% NaCl solution at 25 °C and carbon steel alloy coated with aluminum has been studied , as shown in figures (8) and (9). The potential was measured every one minute for the first ten minutes , then 5 minutes for the remaining time. The potential generally changed from an initial high negative value -460mV (SCE) to amore negative–635mV (SCE) $\pm$ 2mV within about 20 minute and then potential remained stable at this value , -635 mV (SCE), for about three hours as shown in figure (8).

In figure (9), the potential also was measured every one minute for the first ten minutes, then 5 minutes for the remaining time . The potential generally changed from an initial high negative value -632mV (SCE) to a more negative–723mV (SCE) $\pm$ 2mV within about 20 minute and then, potential remained stable at this value , -723 mV (SCE), for about three hours. This indicates a slight potential fluctuation around this value (-723mV) . Corrosion products are deposited on the surface. They were removed from the surface by washing the specimen during optical microscope observation.

The reason for this variation with time depends and is affected by many parameters (i.e., material purity , surface treatment, oxygen content, etc). Corrosion products are also revealed on the surface.

The open circuit potential depends on the presence of oxygen and chloride ions, but not to a great extent on the concentration [11].

3.2.1 Electrochemical Measurements:

The electrochemical behavior of carbon steel, aluminum and aluminum coated steel were studied in NaCl solution. Test specimens were polarized from -1000 mV up to 200 mV at sweep rate of 20 mV /min.

The potential log current density plots obtained for polarization different specimens of uncoated , coated carbon steel and aluminum 3.5% NaCl solution are shown in figure (10) , (11) and (13) . The general shape is the same in all cases , although differences exist is the same in the values of the corrosion potential and corrosion current density as shown in table (4) . Examination of the plots and using tafel extrapolation method for obtaining amixed potential theory principle [14]. The corrosion potential for three polarization curves are very close to the open circuit potential after almost three hours .

Sherif and Narayan [13] have suggested in their study that the open circuit potential of aluminum like those of other corroding metals , is a mixed potential .

Equilibrium that controls this mixed potential includes:

1. Cathodic Reactions:

(a) Reduction of dissolved oxygen

(i) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (3)

(ii) Reduction of H^+ ions:

$2H^+ + 2e \rightarrow H_2 \uparrow$ (4)

The reduction of dissolved oxygen may be occurred during the later immersion period which indicated a deposition. This deposition may be Feo oH [14] , which gave rusted colour to the solution . While hydrogen reduction occurred during all polarization of uncoated specimen is:

$Fe \rightarrow Fe^{2+} + 2e$ (5)

This iron ions are combined the hydroxyl ions to give the rust deposition as mension above.

The anodic reaction for aluminum and carbon steel coated with aluminum are as follow [15] :

a. $Al \rightarrow Al^{+3} + 3e^-$ (6)

b. $Al + 3OH^- \rightarrow Al(OH)_3 + 3e^-$ (7)

c. $Al + 3Cl^- \rightarrow AlCl_3 + 3e^-$ (8)

d. $2Al + 3H_2O^- \rightarrow Al_2O_3 + 6H^+ + 3e^-$ (9)

The formation of aluminum oxide film indicates the reduced in corrosion current density as shown in table (4).

From corrosion current density obtained in table (4), an improvement in corrosion current density was found to be 98.33% for coated specimens. This efficiency improvement was calculated from the following equation:

$$\text{Efficiency improvement in incurrent density (C.D)} = \frac{C.D(uncoated) - C.D(coated}{C.D(uncoated)} \times 100 \quad (10)$$

The nature composition of carbon steels is a limited alloy content , unfortunately , these levels of addition do generally produce any remarkable change in general corrosion behavior. The possible exception to the above statement would be weathering steel, in small addition of copper , chromium , nickel and phosphorus produce significan reduction in corrosion rate in certain environments [16]. This statement agrees with carbon steel analysis shown in table (1) which indicates the disappearance of the above elements and the corrosion rate of carbon steel in 3.5% NaCl is relatively high. The carbon steel specimens indicates the presence of pits as black spots as shown in figure (13).

The aluminum coating that is formed is not homogenous and typically contains a certain degree of porosity and also will contain aluminum oxide. Therefore, the coated specimen illustrate pitting corrosion on the surface as shown in figure (14).

Clearly, aluminum and carbon steel coated with aluminum also suffer from pitting corrosion much less than carbon steel as shown in figures (13) and (14). The U.S navy are frequently used aluminum coatings for corrosion protection of many ship components [17].

From these tests, it is concluded that Al- protects carbon steel in NaCl from pitting corrosion but the Al-dissolution rate is actually important, essentially due to the effect of galvanic corrosion with carbon steel, which is due to coating defects as shown in figure (7).

Pitting corrosion in carbon steel coated with aluminum is due to the coating defects such as porosity. This corrosion problem is a galvanic corrosion type at the interface between carbon steel and aluminum coated. The pitting density which appeared in carbon steel coated with aluminum is much less than carbon steel specimens as shown in figure (13 and 14). This indicates that carbon steel coated with aluminum has improved corrosion resistance. This improves the resistance of marine environments.

Conclusions

From the results obtained in the present work the following conclusions can be drawn:

Corrosion rate test specimens of carbon steel immersed in sea water is much higher than that of specimens coated with aluminum. An improvement efficiency range of 86-91.5% is obtained during the immersion periods of 5-20 days.

1- The corrosion potential for uncoated specimens is higher than that of coated specimens which indicates that aluminum coats used as sacrificial anode to protect the alloy.

2- Aluminum coating sealed by epoxy coat closes the porosity which occurred during thermal spray method .This also improves the corrosion resistance of the carbon steel.

3- Corrosion current density for carbon steel coated with aluminum is much less than that for carbon steel which indicates an improvement in corrosion resistance. An improvement efficiency in corrosion current density is found to be 98.33%.

4- The pitting density appears more clearly in carbon steel alloy than carbon steel coated with aluminum.

References

1. Tomashov N.D.,"Theory of Corrosion and Protection, the Macmillan Company, New York,1966.

2. J. Creus, H.Idrissi, M. Mazille, laboratorie de physico-chimie Industrielle, INSA Lyon, Villeurbanne, France.

3. www. West. Wesrcoast Corrosion . Com / service 20 % anode 20 % protecction . htm . 2004.

4. www. West Coast corrosion. com / cathodic 20 % protection history . htm . 2004.

5. Bull. Mater . Sci. , vol . 24, No. 4 , Augest 2001 , p 335-360 . China.

6. ASTM , Metalhand book , 9th edition , vol. 1 , 739 , 1990.

7. Epikotes , Techinical Manual 2nd edition , 1999.

8. Avner , G. , "Introduction to physical metallurgy" , 1967.

9. أطروحة ماجستير ، إسراء قحطان صبري ، هندسة المواد . كلية الهندسة ، جامعة بابل ، 2000.

10. Latha G. and Rajes Wari , vol. XIII , No. 6 , 2000.

11. Dibari G. A. , and Rend H.J. , Corrosion , vol. 27 , No. 11 December , 1971.

12. http : // www. Corrosion source com. / learning centre / pitting htm . 2004.

13. Sherif , K.P. , and Narayan R. , Br . Corrosion J. vol. 24 , No. 3 , P 199 , 1989.
14. http / www . corrosion sience . htm . 2004 .
15. Huang. T. S. and Frankel G.S. , "Localized Corrosion Growth Kinetics in AL alloy " 19 Sept. 2002, www. Corrosion doctor / search / new search / AL corrosion / htm L .
16. Knowledge Article from www. Key to steel com., "Corrosion of Carbon Steel", file: // D: \ SFI \ Corrosion 20 % carbon 20 % steel. htm, 21/09/1425.
17. Thermal spray fundamental, EM 1110-2-3401, 29 Jan., 1999, http: // www. Usace / army / mill.

Table (1) Chemical composition of Carbon Steel (in wt%).

Element	Specialized Institute of Engineering Industries	DIN Standard
C%	0.198	≤0.2
Si%	0.4815	≤0.55
P%	0.0304	0.05
S%	0.0262	0.05
Cr%	-	-
Mn%	1.21	≤1.50
Cu%	-	-
Fe%	Pure	Pure

*DIN : Standard Germany specification unit.

Table (2) Shows the specification of epoxy[7].

Property	Test Method	Value
Epoxy group content	SMS2026	5150-5490 m.mole /kg
Epoxy molar mass		182-194 g /mole
Viscosity at 25 °C	ASTM D445	9-14 pa.s
Color	ASTMD1544	3 max. Gardner Scale

Table (3) Weight loss and corrosion rate measurements for carbon steel alloy and Carbon steel alloy coated with aluminum in 3.5% NaCl.

Time (Days)	Weight loss (mg) carbon steel alloy uncoated	Weight loss (mg) Carbon steel alloy coated with aluminum	Corrosion Rate (mdd) carbon steel alloy uncoated	Corrosion Rate (mdd) Carbon steel alloy coated with aluminum	Efficiency of corrosion rate %
5	7.225	0.999	20.642	2.857	86.2
10	14.125	1.1999	20.785	1.714	91.5
15	21.07	1.799	20.07	1.713	91.5
20	24.54	2.39	17.529	1.707	90.0

Table (4) Results obtained from electrochemical tests.

Material sample	E_{corr}(Mv)	I_{corr} (A/cm^2)
Carbon steel	-635	$6X10^{-5}$
Pure Aluminum	-719	$7X10^{-7}$
Al-coated carbon steel	-723	$1X10^{-6}$

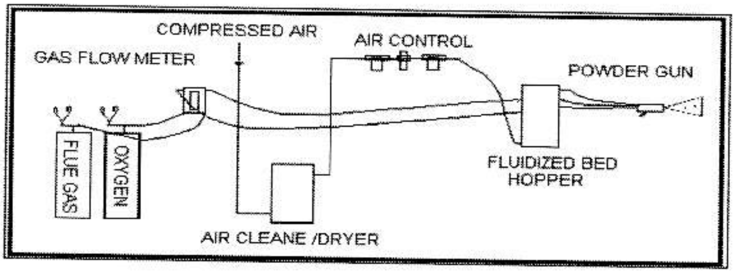

Figure (1) Typical Combustion Powder Gun.

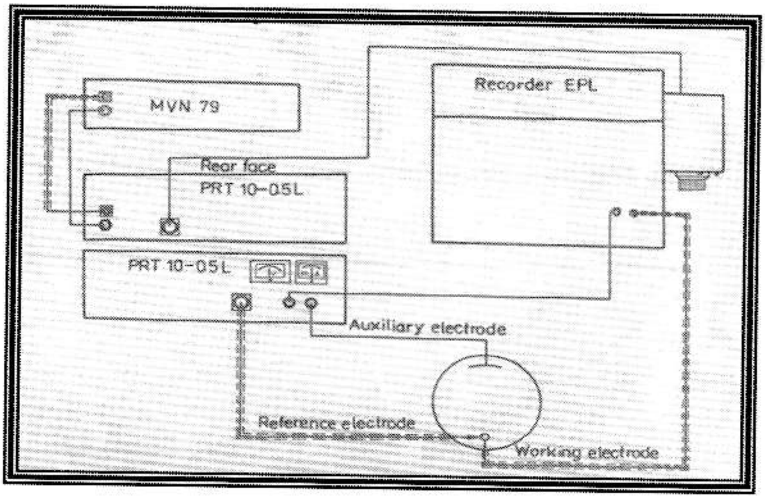

Figure (2) Electrical Circuit Connection.

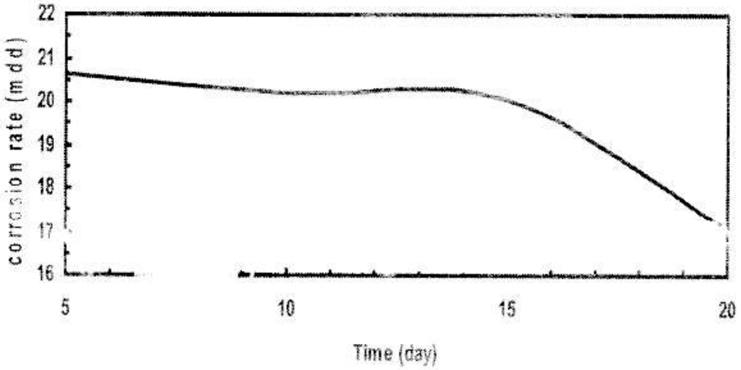

Figure (3) Represents the corrosion rate with time for carbon steel (ST-52).

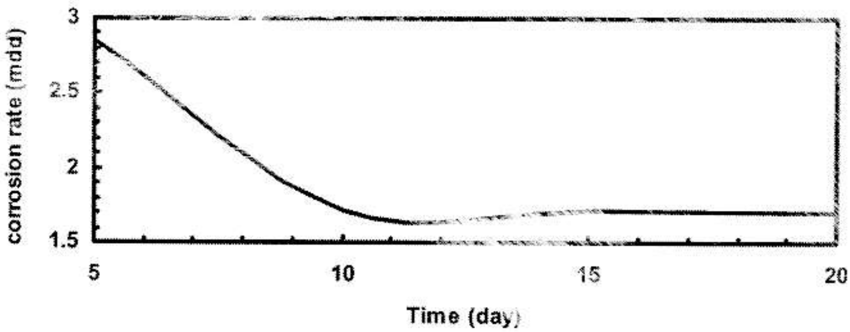

Figure (4) Represents the corrosion rate with time for carbon steel (ST-52) coated with aluminum.

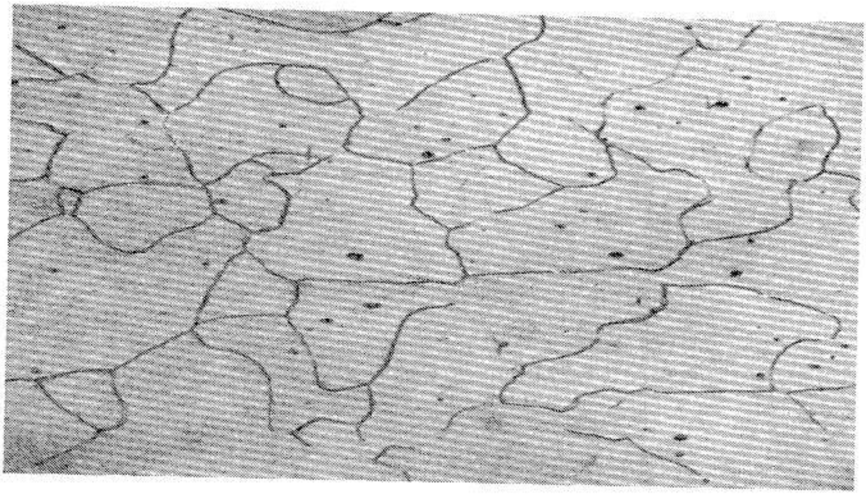

Figure (5) Microstructure of carbon steel alloy etched with 5 percent nitric acid in alcohol.

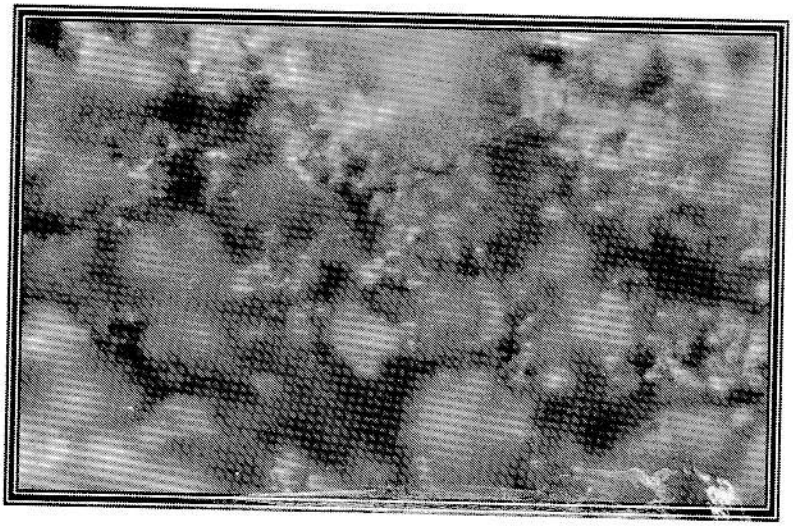

Figure (6) Represents the carbon steel alloy coated with aluminum

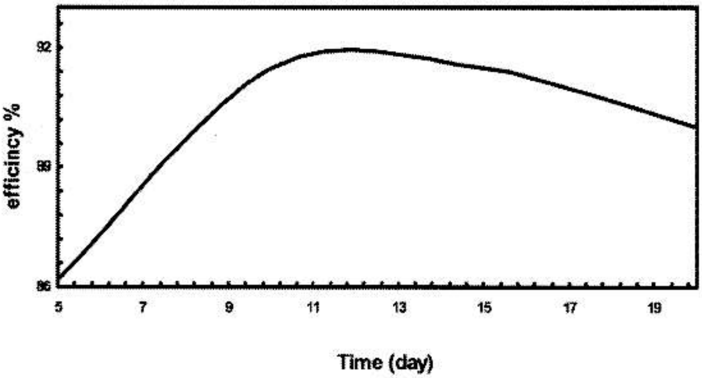

Figure (7) Represents the relation between efficiency and time.

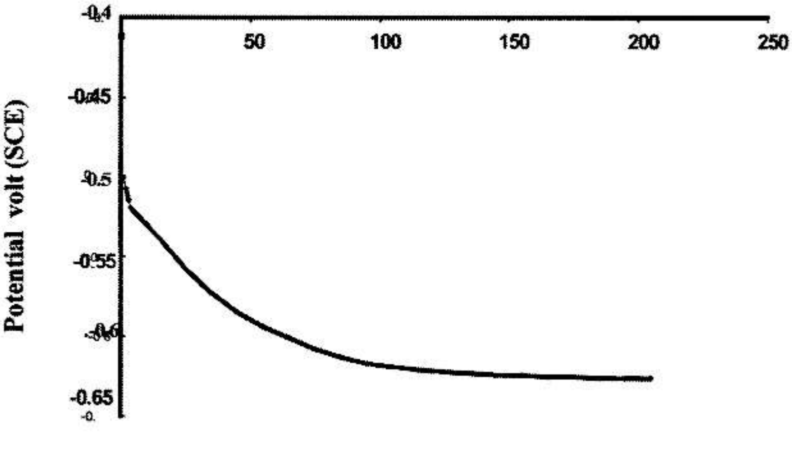

Figure (8) Represents free corrosion potential of carbon steel alloy (ST-52-3RR) .

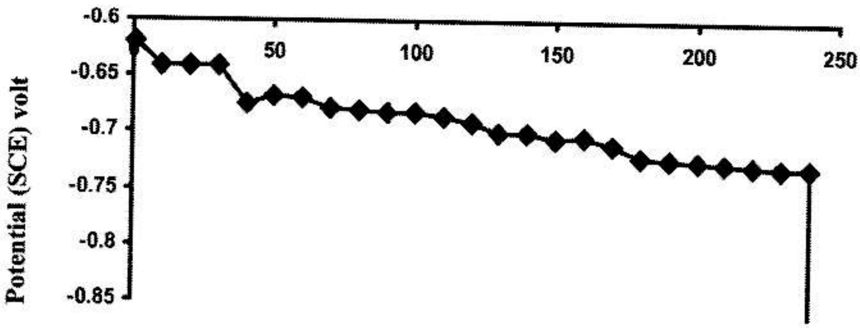

Figure (9) Represents free corrosion potential of carbon steel coated with aluminum .

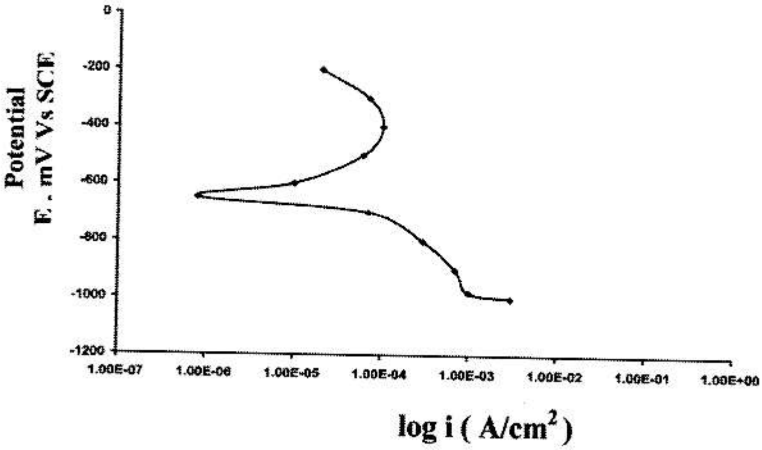

Figure (10) Polarization curve of carbon steel in NaCl solution at 25 °C.

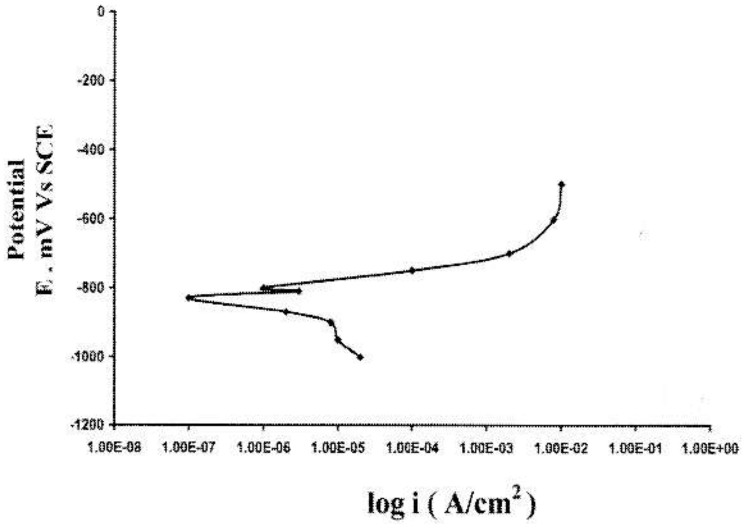

Figure (11) Polarization curve of aluminum in NaCl solution at 25 °C.

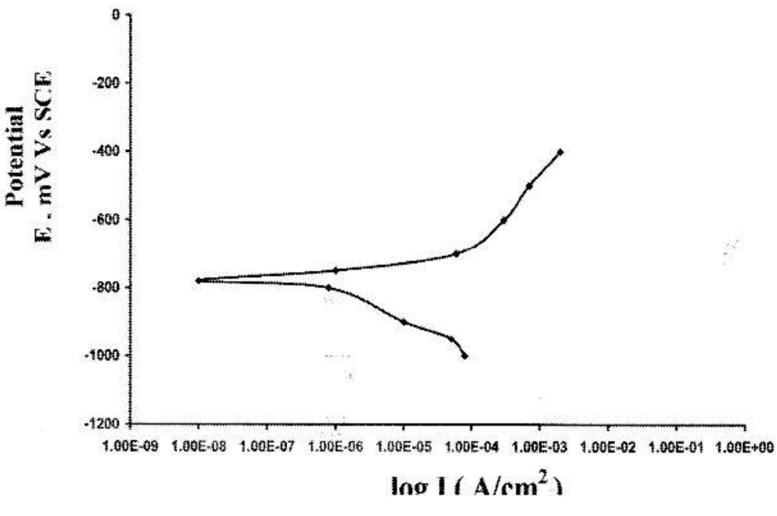

Figure (12) Polarization curve of aluminum coated in NaCl solution at 25 °C.

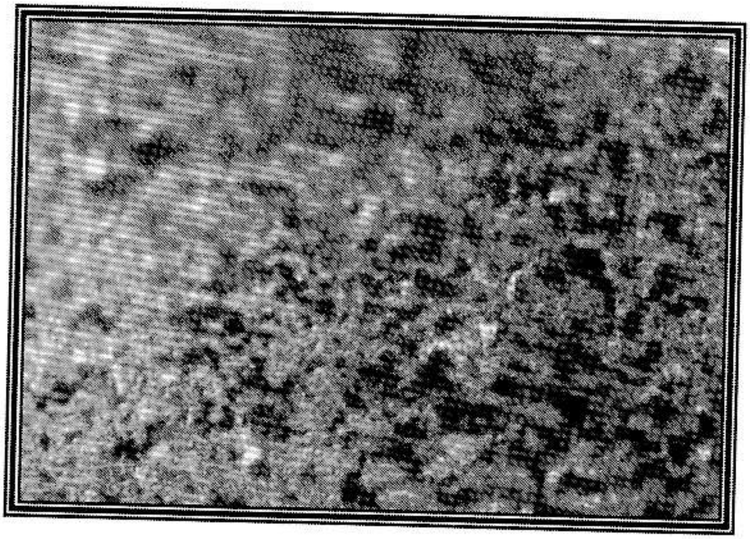

Figure (13) Represents the carbon steel alloy showing pitting corrosion (200X).

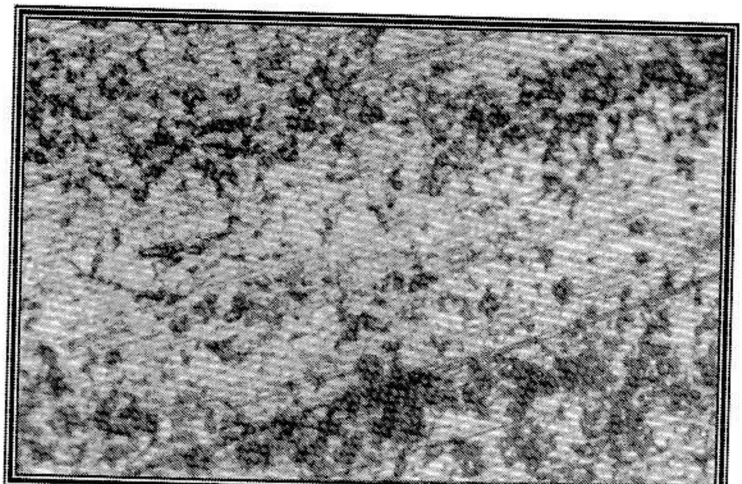

Figure (14) Represents carbon steel alloy coated with aluminum with pitting corrosion.(200X).