Study Corrosion Behavior of Low Carbon Steel coated by Sherardizing and Polypyrrole Polymer

Assist .Prof .Dr. Sihama I. Al-Shalchy[*], Prof. Dr. ALI H. Ataiwi [**], Gufran Abdul Mahdi[***]

[*]**Department of Materials Engineering, University of Technology**
*Sihama_Salih@yahoo.com

**ali.alomairy@uokufa.edu.iq

***Gufranmaterials@yahoo.com

Abstract

Oil pipelines low carbon steel were coated by sherardizing process at $400^{o}C$ for different times (15, 30, 60, 120, 240 min), then some samples of the sherardizing was coated by polymer conductive polyprrole, The results of this research showed that the thickness of sherardizing coated was increasing as time treatment was increased. The corrosion performance of sherardizing and polypyrrole coated steel was evaluated by polarization and scanning electron microscope (SEM) .The results show that the presence of polypyrrole and sherardizing coatings significantly increase the corrosion resistance and drastically reduces the corrosion current and corrosion rate of steel.

Keywords: Polypyrrole; sherardizing; Low carbon steel; Electrochemical polymerization; Corrosion resistance.

Introduction

Corrosion is chemical interaction between a metal and its environment which results in changes of the metal ' s properties and which may lead to significant functional impairment of the metal, the environment or the technical system of which they form a part. The corrosion processes begins when a corrosive medium acts on a material. Two kinds of corrosion reactions are distinguished:

• Chemical corrosion: Corrosion excluding electrochemical reaction.

• Electrochemical corrosion: Corrosion including at least one anodic and one cathodic reaction in passive corrosion protection, corrosion is prevented or at least decelerated through the isolation of the metal material from the corrosive agent by the applied protective layers [1].

In Zinc powder coating, the protection method for which coating materials pigmented with zinc powder are applied onto steel components as protection layers.Sherardizing is the coating of iron or steel with zinc/iron alloy. Items are slowly rotated in the presence of zinc dust, and an inert operating medium, for a few hours at temperatures of 320-500°C, often about 385°C. The zinc dust can pass through a 75micron sieve. The dual role of sherardizing in the protection of steel, a sherardized coating inhibts the corrosion of steel in two basic ways:

1-the formation of a protective film.

2-the sacrificial role.

Zinc corrodes much more slowly than steel in most natural environments. The formation of protective film on zinc during exposure are mainly responsible for its excellent resistance to atmospheric Corrosion [2-7].

But in the use of conducting polymer such as polypyrrole as anti-corrosion coatings, this polymer act as anodic protection and significantly reduce the rate of corrosion. However, the use of conducting polymers in the protection of metals is hindered by their insolubility in common solvents. These polymer cannot be processed by spin or dip coating. This drawback can be overcome by electropolymerization which can simultaneously form and deposit polymer coatings on the substrate from a monomer–electrolyte solution. Polypyrrole has been successfully electrodeposited onto inert metals. However, aqueous electropolymerization of pyrrole onto reactive metals such as steel, zinc and aluminum, has not been very successful because of the preferred dissolution of these metals [8-10]. Jing Hua Jiang *et al.*[11] studied zinc protective coatings on high carbon SWRH82B-1 high-strength steel bridge cable wires (SBCW) sherardized to markedly improve corrosion resistance. Sherardizing parameters were optimized by the optical microscopy (OM) /scanning electron microscopy (SEM), X-ray diffraction (XRD) and potentiodynamic polarization tests. Additions of Y_2O_3 activator were made for sherardizing coating to slightly increases the corrosion resistance of sherardized steel wire in comparison with CeO_2.

T. *Zhang and C.L. Zeng*[12], investigated the electrically conducting polypyrrole (PPY) coatings doped with sodium dodecylsulfate (SDS) have been deposited on 1Cr18Ni9Ti stainless steel by anodic polymerization from aqueous solutions of

pyrrole and sodium dodecylsulfate. The corrosion behavior of PPY coated steel was investigated in 0.3M HCl aqueous solution at room temperature by a combination of electrochemical measurement techniques and scanning electron microscopy. Fifty-day exposure experiments indicated that the PPY coating shows high stability, and can inhibit effectively the corrosion of the steel.

Experimental part

Material :

Low carbon steel pipe was taken from the pipelines of the Midland Refineries Company for high temperature service type A 106, made according to an American society for testing and materials (ASTM) and was supplied by Daura refiner. Table (1) gives the chemical composition of low carbon steel which was used in this search.

Table (1): Chemical composition of low carbon steel.

Element	C	Mn	Si	S	P	Fe
Wt %	0.195	0.460%	0.215%	0.0173%	0.0107%	Balance%

Zinc powder with a purity of about 99.9%, whose chemical composition is shown in Table (2), was used for coating.

Table (2): Chemical composition of zinc powder.

Iron (Fe)	Heavy metals	Arsenic(As)	Cadmium(Cd)	Tin(Sn)	Zinc
0.005%	0.01%	0.00001%	0.005%	0.001%	Balance%

The particle size analysis of zinc powder was carried out in a laser diffraction, particles size analyzer type (SHIMADZU SAID -2101) was used. The result of particle size distribution is shown in Figure (1). The mean diameter for the zinc particles was (29.317) μm and the medium value was (31.686) μm.
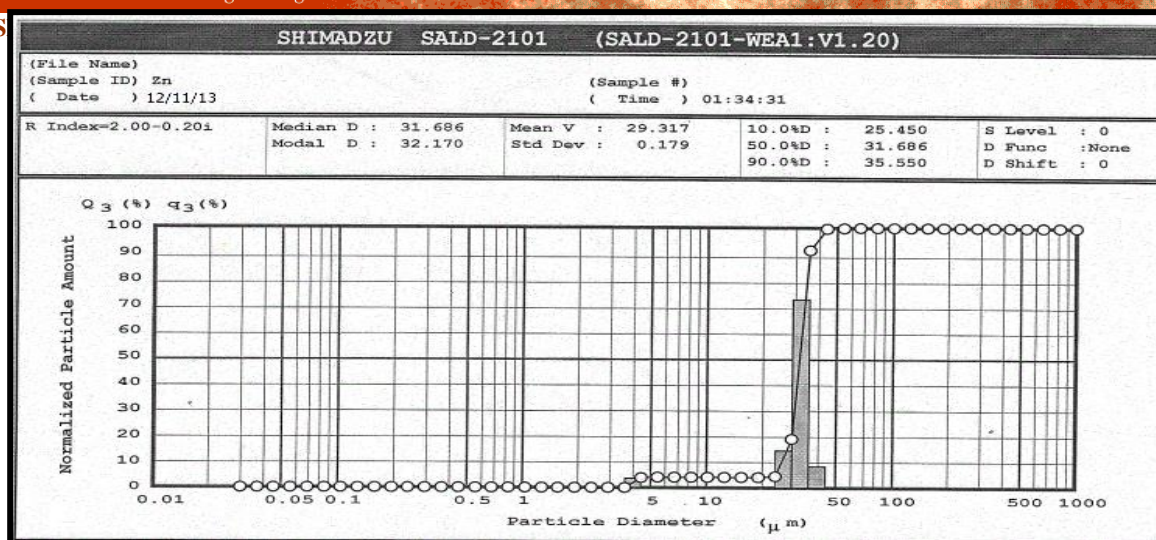
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                    SHIMADZU   SALD-2101    (SALD-2101-WEA1:V1.20)
(File Name)
(Sample ID) Zn                              (Sample #)
( Date   ) 12/11/13                         ( Time  ) 01:34:31
R Index=2.00-0.20i    Median D : 31.686   Mean V  : 29.317   10.0%D :  25.450    S Level  : 0
                      Modal  D : 32.170   Std Dev :  0.179   50.0%D :  31.686    D Func   :None
                                                             90.0%D :  35.550    D Shift  : 0
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Figure 1: Particles size distribution of zinc powder

The sand used is Iraqi silica sand from Al-ardhimah region. Its chemical composition is shown in Table (3), the analysis was done by using atomic absorption spectrophotometer type Unicom England.

Table (3): The chemical composition of the Al-ardhimah sand.

SiO2%	CaO%	MgO%	Al2O3%	Fe2O3%	SO3%	Cl %	Na2O3	K2O%
97.85	0.56	0.06	1.06	0.16	trace	0.04	0.12	0.15

The particle size of sand is in the range (250-100) μm.

The pyrrole was used in this research have the properties are shown in Table (4)

Table (4): Properties of pyrrole

Pyrrol	Liquid	C_4H_5N	Fluka	99%

Surface preparation is the essential for coating purpose ,as the first stage treatment of a substrate before the application of any coating, low carbon steel pipe was prepared by cutting the pipe to samples according to inspection used and then cleaning by using hydrochloric acid (HCL) in

20% to remove outer oxide layer(its formed after annealing process at 800C° for 2 hour) and to obtain clean surface, Then the samples are washed by water and equaled the acid with sodium hydroxide (NaCl) then washed with water again , the work surface of samples was abraded with silicon carbide abrasive paper down from 320 grit to 8oo grit to obtain surface smoothly , then the samples rinsed with de ionized water and degreased in acetone. Then coating was begun directly to avoid samples oxidation which might cause Failure of coats.

- **Sherardizing process**

The sherardizing process was done by mixing zinc powder with sand at ratio (50:50) % for a period of 15minutes period. The samples and mixture are placed together inside containers, then these containers are closed and placed inside furnace at 400 C° for different treatment times (15, 30, 60, 120, 240 min). Finally the coated samples are cooled to room temperature inside a switched off furnace.

- **Coating by conductor polymer (PPY)**

This coating done by using pyrrole material, The electropolymerization was carried out in 0.1 M monomer of pyrrole (99% Fluka) plus 0.25 M oxalic(99% Fluka) acid as dopant electrolytes in distilled water. Electropolymerization was done in three electrodes system. A platinum electrode and a silver/silver chloride (Ag^0/Ag^+) were used as counter and reference electrode respectively. The working electrode was made of carbon steel ,polypyrrole (PPY) were electropolymerized onto an electrodes by cyclic voltammetry with a scan rate of 40 mV/s. All the electropolimerization reactions were carried out in the scan range of -100 to 2000 mV versus (Ag^0/Ag^+).

Inspection

Microstructure Test: has been accomplished on cross section of samples (low carbon steel and sherardized samples), with magnification range of 500X. This test was done by using optical microscope type (Reflected metallurgical microscope (XJL-101).

Coating Thickness Measurement: The thickness of coating was measured after sherardizing process by using automation machine, average of five readings were taken for each sample.

Electrochemical Test: Electrochemical methods were used in this work to determine corrosion parameters which involved E_{corr}, i_{corr} and corrosion rate, by using potentiostat instrument.

Scanning Electron Microscopy Test: Scanning electron microscope (SEM) with a field emission gun operating at 30 KV, was used to assess the microstructure of samples.

Results and Discussion:

Microstructure: The microstructure of the surface of low carbon steel before and after sherardizing coating are shown in Figures (2 a and b). Microstructure of sherardizing coating, Figure 2 (c and d), respectively shows that the coating thickness at (15, 240 min) respectively. Microstructure characterization of sherardizing coating does not show a distinct crystal structure (unlike hot dip galvanizing where coating is formed initially by solidification from a melt) [3].
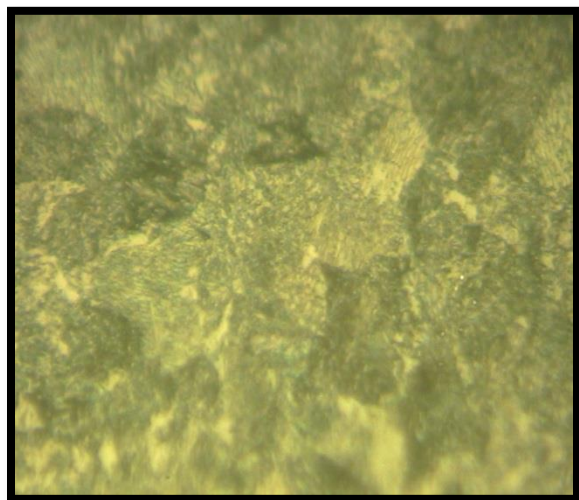
(a) Low carbon steel as received
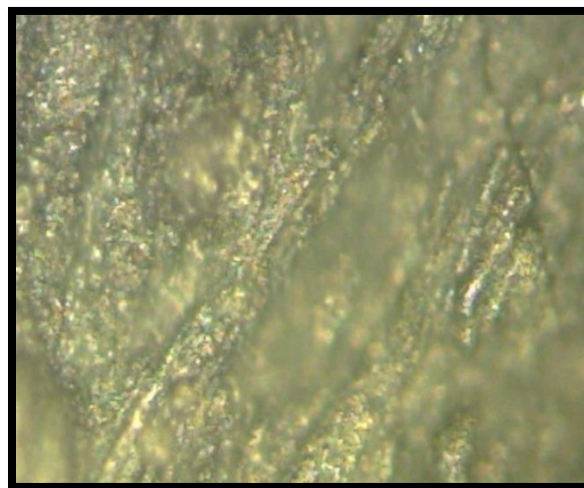
(b) sherardizing surface
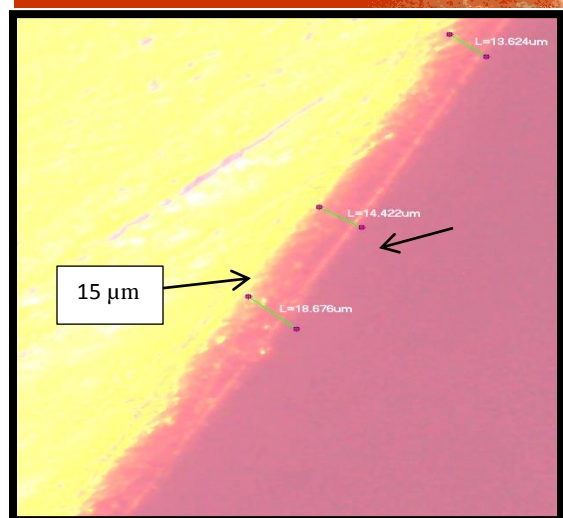
(c) Sherardizing thickness at 15 min
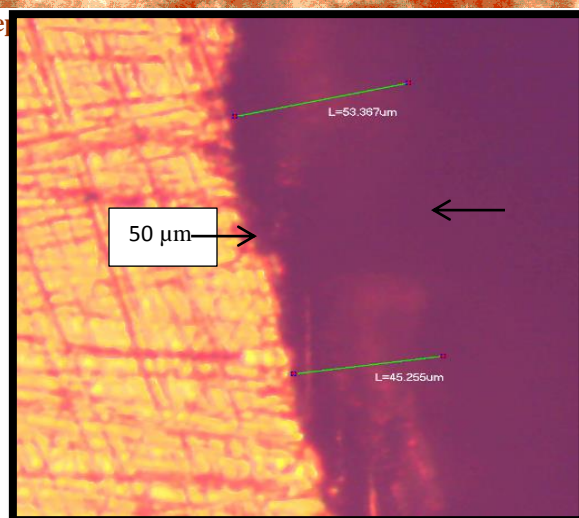
(d) Sherardizing thickness at 240 min

Figure 2: Optical micrographs of surface of (low carbon steel) samples before and after sherardizing coating.

The sherardizing coating thickness increases with treatment time as shown in Figure (3) .The coating thickness increases from 21µm to 52 µm when treatment time increased from 15 min to four hours at 400°C. That is due to increment of diffusion of zinc powder with coating time [5].
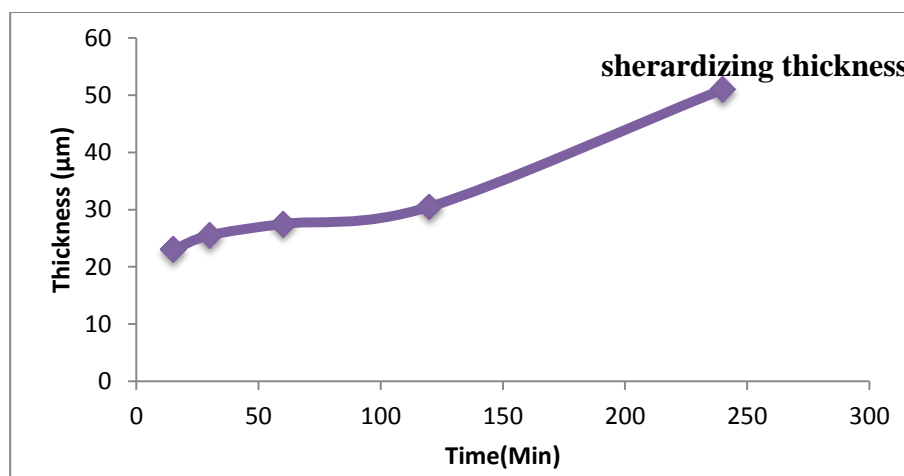

Figure 3: sherardizing thickness as a function of treatment time.

The corrosion behavior of sherardizing coatings were analyzed by polarization studies and the polarization curves are displayed in Figure 4 at pH=6.9. This figure compare corrosion resistance of the substrate (low carbon steel (as received)) with sherardizing coatings and polymer conductive coatings specimens. The corrosion current density is an important parameter used for evaluating the kinetics of the corrosion reaction. Corrosion protection is inversely proportional to the corrosion current density. The difference between polarization curves is mainly due to corrosion current density and indicates that corrosion reactions take place continuously at the interface and the coating bonding state at the substrate keeps changing during the corrosion test. Theoretically, higher corrosion potential means lower electrochemical activity and then higher corrosion resistance. Higher thickness and lower porosity in microstructure of sherardizing coating lead to an increase in corrosion resistance of the coated samples because both higher thickness and lower porosity provide stronger diffusion resistance to prevent the oxidant corrosion electrolyte from reaching the interface of the coated samples.

The electrochemical parameter −corrosion current density i_{corr} which was obtained from potentiodynamic polarization tests are listed in Table 5 for all samples in pH=6.9. The corrosion current density i_{corr}, for the as received sample (without coaying) is found to be 32.9 $\mu A/cm^2$, while the incorporation of sherardizing coat reduces the corrosion rate to less the half value at 4hr, which means that the coatings by sherardizing has improved the corrosion resistance. The high value of corrosion resistance for a sherardizing coat may be due to the high thickness of the sample. Calculation of corrosion rate from the corrosion current.

According to Faraday's Law:

$$CR = 0.13\ i_{corr}\ \frac{e}{\rho} \dots\dots\dots\dots\dots (2\text{-}4)$$

where:

CR: Corrosion rate (mil-inches per year),

i: Corrosion current density ($\mu A.cm^{-2}$),

e: Equivalent weight of material (gm),

ρ: Density of material ($gm.cm^{-3}$).

Table 5: Corrosion parameters for coated steel carbon with sherardizing in 3.5 % NaCl, with values and corrosion rate.

Time coating	i_{corr} μA/cm2	E_{corr} mV	CR Mpy
Carbon Steel as received	32.9	-743.9	19.5
Sherardizing (15 Min)	15.44	-662.4	9.16
Sherardizing (30 Min)	5.65	-492.6	3.35
Sherardizing (1 hr)	3.62	-577	2.148
Sherardizing (2 hr)	2.20	-523.7	1.313
Sherardizing (4 hr)	2.07	-880	1.228

Corrosion behavior by conductor polymer coating: The electrochemical parameters –corrosion current density i_{corr} which was obtained from potentiodynamic polarization tests are listed in Table 6 for all samples at pH=6.9. The corrosion current density i_{corr}, for the as received sample coated with polymer conductive (PPY) is found to be 0.206 μA/cm^2, while the incorporation of sample with sherardized coat (at four hours) and PPY reduces the corrosion rate to 0.107 μA/cm^2. As shown in Figure 5.

Table 6: Corrosion parameter for coated steel carbon with sherardizing and polymer conductive in 3.5 % NaCl , with values and corrosion rate.
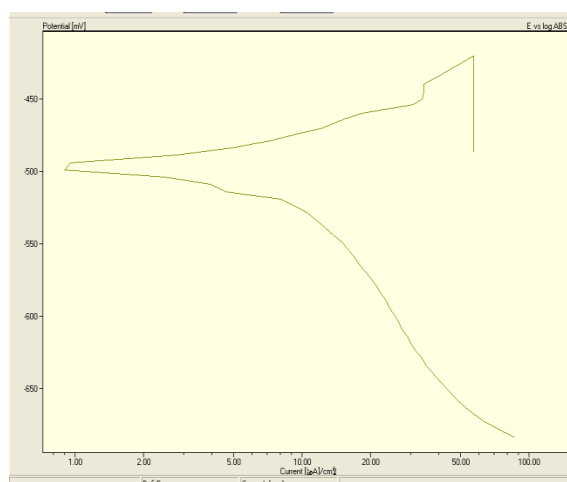
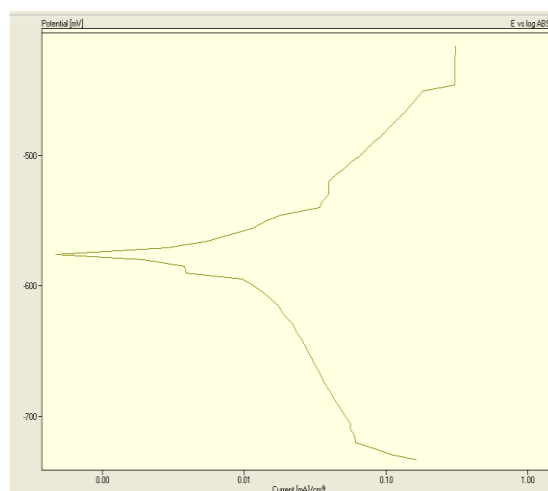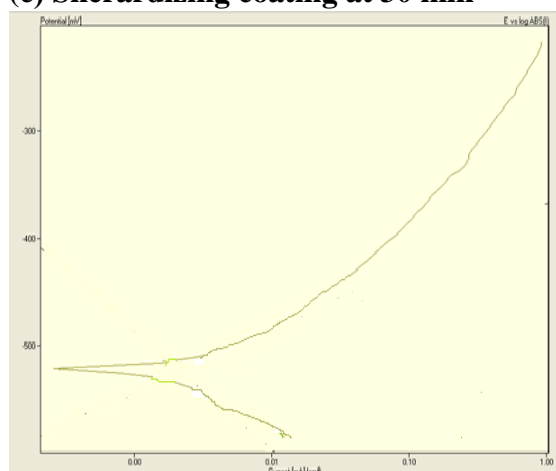| polymer conductive	i_{corr} μA/cm^2	E_{corr} mV	CR mpy
Steel carbon as received	32.9	-743.9	19.5
PPY on steel (as received)	0.2064	-569.3	0.00714
PPY on sherardizing	0.107	-740.9	0.00371
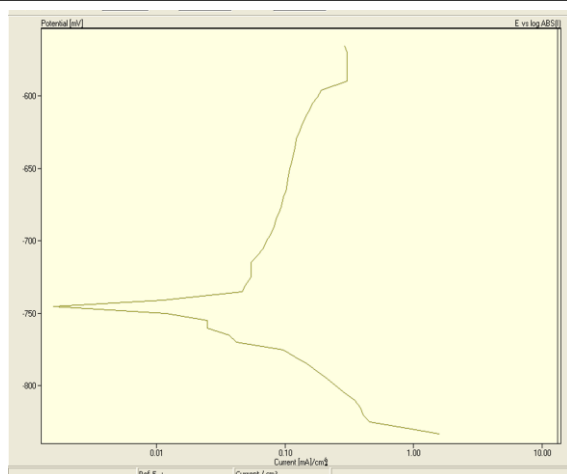
(a) As received low carbon steel
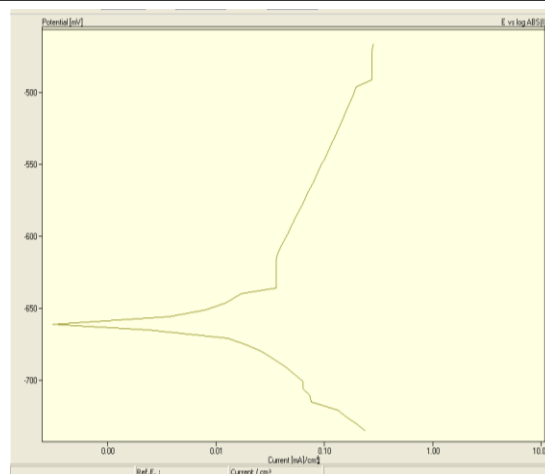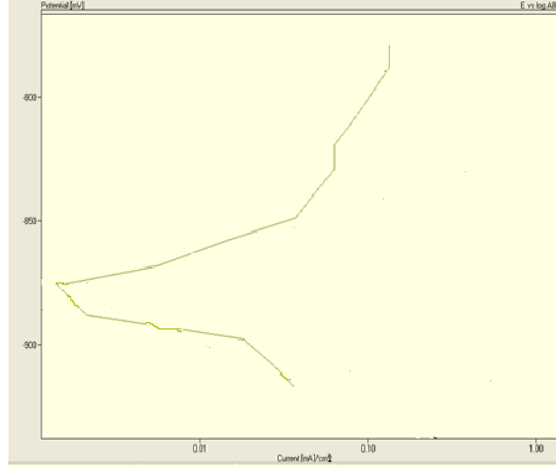
(b) Sherardizing coating at 15 min

(c) Sherardizing coating at 30 min

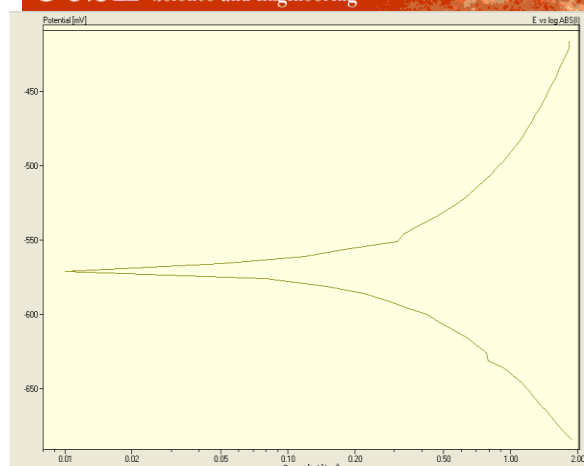(d) Sherardizing coating at 60 min
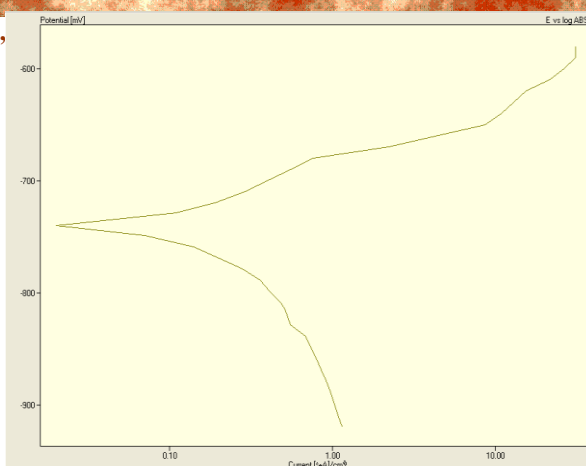
(e) Sherardizing coating at 120 min

(f) Sherardizing coating at 240 min

Figure 4: Potentiodynamic curves in NaCl for as received carbon steel and sherardizing steel at different coating thickness.

(a) PPY on steel (as received)   **(b) PPY on sherardizing coating**

Figure 5: Potentiodynamic curves of PPY in NaCl.

In Figure 6 is shown that the corrosion rate of the polymer conductive coatings (PPY) on low carbon steel without sherardizing coating (as received) is -19.5 mpy while incorporation of PPY and sherardizing gives corrosion rate of 0.00371 mpy, which means that the coatings by polymer conductive and sherardizing together improve the corrosion resistance. The enhancement of corrosion resistance by conductive polymer may be due to the prohibition of electrolyte arrival (NaCl) to the steel surface which results in reduction of galvanic corrosion of steel surface.
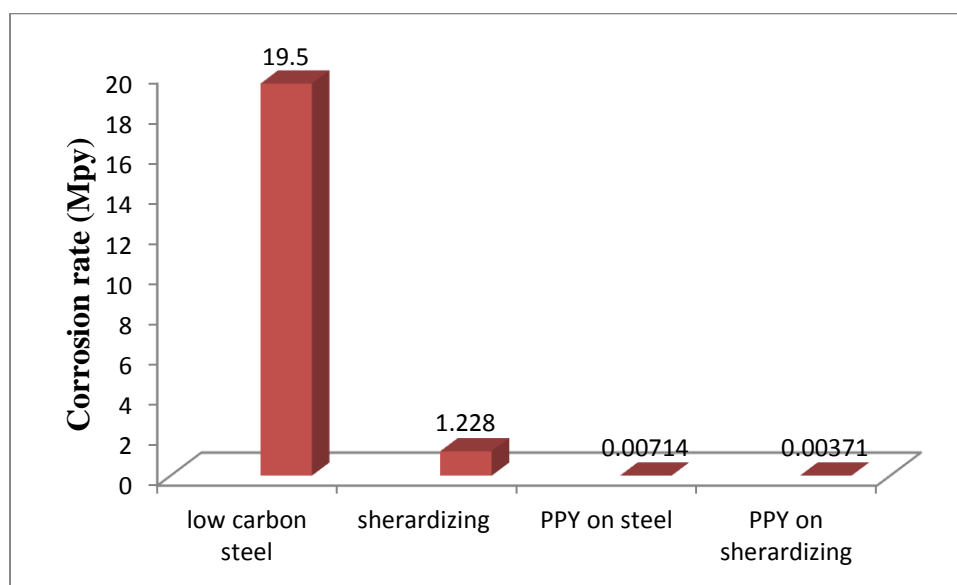

Figure 6: corrosion rate at different coatings**.**

- In Figure 7 shows the surface morphology of the sherardizing coating. And in Figure 7 a, it can be observed that the sherardizing surface coating is at 4 hrs with a surface roughness equal to 2.637 µm. And in Figure 7 b shown The thickness of sherardizing coating for the sample treatment for 4 hrs was observed equal to 51µm.
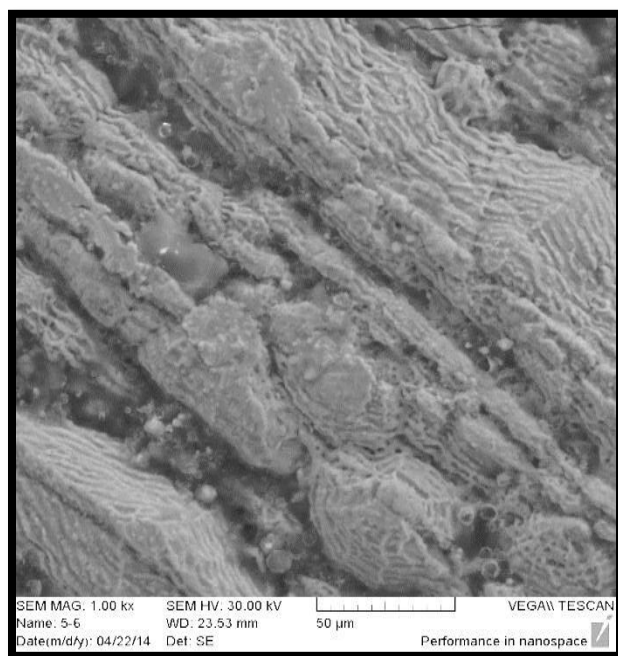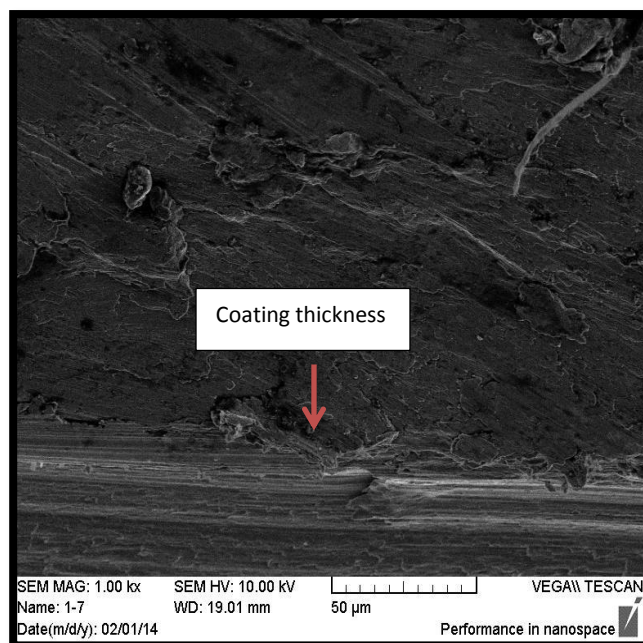
a) 500 X   b) 1.00Kx

**Figure 7:** SEM of sherardizing coating at different magnifications.

Figure 8 shows SEM micrographs of coated steel samples by sherardizing and polypyrrole conductive. The comparison of these micrographs shows cleary the difference in the morphology between polypyrrole conductive over sherardizing coating and polypyrrole conductive over bare steel sample. Figure 8d shows formation of particles of polypyrrole with interconnected network type structure,   the microstructure of the polypyrrole films is not smooth, particles size lying in the range (0.2-2) µm for polypyrrole film coated the low carbon steel substrate bare surface and particle size lying in the range (0.5-2.5) µm for polypyrrole film coated the sherardizing surface shown in Figure 8 d.
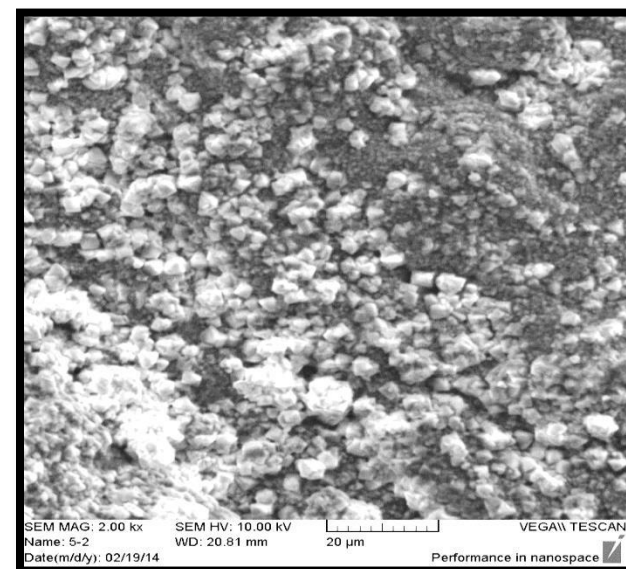
(a) SEM of low carbon steel as received (bare surface).
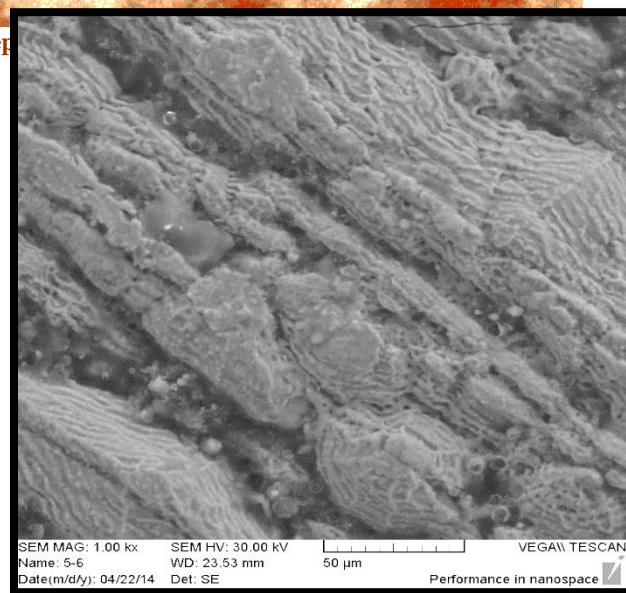
(b) SEM of sherardizing surface at 4 hr.
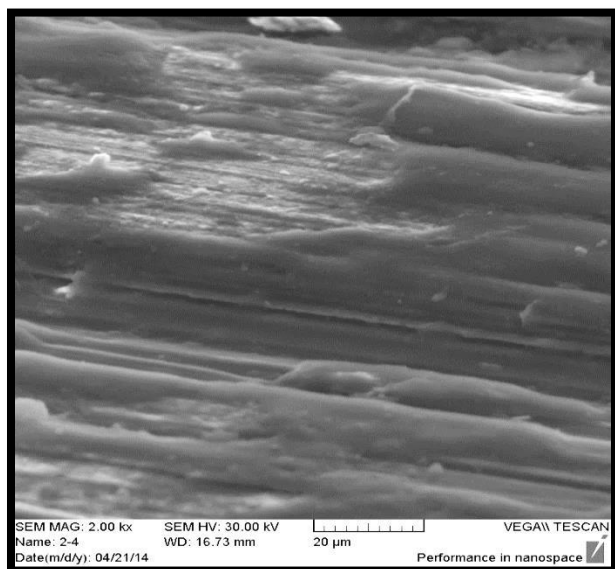
(c) SEM of PPY films on as received low carbon steel.

(d) SEM of PPY films on as sherardizing surface

Figure 8: **(**a) SEM of low carbon steel as received (bare surface) at 1000x , (b)SEM of sherardizing surface at 4 hr at 1000x, (c) SEM of polypyrrole films deposited on as received low carbon steel at 2000x and (d) SEM of polypyrrole films deposited on sherardizing coating at 2000x.

Oil pipelines low carbon steel were coated by sherardizing process at $400^{o}C$ for different treatment times then the sherardizing samples were coated by polypyrrole, the corrosion resistance was conducted in NaCl (PH 9.6) and analyzed by polarization The following conclusions are obtained:

1- Microstructure characterization of sherardizing coating does not show a distinct crystal structure.

2- The sherardizing coating thickness increases with treatment time. The coating thickness increases from 21µm to 52 µm when treatment time increased from 15 min to four hours.

3- The corrosion current density (i_{corr}) and corrosion rate values are (32.9 µA/cm^2) and (19.5mpy), respectively for as received sample (bare surface), whereas the incorporation of sherardizing coat for 15 min reduces (the i_{corr}) to 15.44 µA/cm^2 and corrosion rate to 9.16 mpy increasing the sherardizing treatment time to 4hrs decreased the i_{corr} to 2.07 µA/cm^2 and corrosion rate to 1.228 mpy. This means that coating the sample by sherardizing has improved the corrosion resistance of low carbon steel.

4- Coating low carbon steel with bare surface by PPY conductor polymer lowered the i_{corr} and corrosion rate values to (0.2064 µA/cm^2 and 0.00714 mpy), respectively, which are much smaller as compared to low carbon steel and sherardizing coating samples.

5- Coating the sherardizing low carbon steel by PPY conductor polymer much lower the i_{corr} and corrosion rate to (0.107 mpy) and (0.00371mpy), respectively as compared to sherardizing coating samples for 4hrs at 400°C which were (2.07 µA/cm^2) and (1.228 mpy), respectively.

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