

S.I. SalihMaterials Eng. Dept.,
University of Technology,
Baghdad, Iraq.Sihama_salih@yahoo.com**A.H. Ataiwi** College of Engineering.,
University of Kufa, Najaf, Iraq.ali.alomairi@uokufa.edu.iq**G.A. Mahdi**Materials Eng. Dept.,
University of Technology,
Baghdad, Iraq.Gufranmaterials@yahoo.com

Corrosion Protection of Carbon Steel by Zn/PPY mCoating as Layers in 3.5% NaCl

Abstract- Plate from low carbon steel was took from oil pipelines, and coated with two layers, the first layer was done by sherardizing process at 400°C for variable periods (15, 30, 60, 120, 240)min, the second layer was applied by polypyrrole (PPY). The results showed that the thickness of sherardizing layer paint is increased when increasing treatment time (15, 30, 60, 120, 240 min). The corrosion performance was evaluated by using polarization method. In addition, it was examined morphological surface of paint layers by using scanning electron microscope (SEM). The results showed that the presence of polypyrrole layer with sherardized coatings, showned significantly increase in corrosion resistance, and coating of low carbon steel by using polypyrrole the conductive polymer with sherardizing process, drastically reduced from the corrosion current density values, as well as the corrosion rate of low carbon steel. The corrosion rate of the 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.

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

How to cite this article: S.I. Salih, A.H. Ataiwi, and G. A. Mahdi "Corrosion Protection of carbon steel by Zn/PPY coating as layers in 3.5% NaCl," Engineering & Technology Journal, Vol. 35, No. 8, pp. 821-830, 2017.

1. Introduction

Corrosion affects the metal because of a chemical or electrochemical reaction with its environment, which results the degradation of the material or its properties because of its interaction of two or more substances or their components in the presence of an auxiliary medium such as salts, heat or humidity. Corrosion processes begins when corrosion occurs on a material. Two types of corrosion reactions are distinguished: chemical corrosion and Electro-Chemical corrosion.

Chemical corrosion arises due to direct interaction between the metal or the alloy with its related environment. Whereas electrochemical corrosion is caused by an electric current exposed to the metal as a result corrosion resulting from galvanic interaction or shed external voltage Electro-Chemical corrosion: Corrosion excluding electrochemical reaction.

Corrosion protection: to prevented corrosion or at least slowed down, by insulating the metal material from the corrosion agents, through the work of the protective layers [1].

The one of the ways of protect is a zinc powder coating, where coating materials with zinc powder are applied onto metal materials as a protection layers. Sherardizing is the coating of iron or steel with zinc/iron alloy. The zinc dust can pass through a 75-micron sieve. The dual role of sherardizing in the protection of steel, a

sherardized coating inhibits the corrosion of steel in two basic ways:

- 1-the formation of a protective film.
- 2-the sacrificial role.

Zn is more action than steel so that, it corrodes more than steel. The formation of protective film of zinc during exposure are mainly responsible for its excellent resistance to atmospheric Corrosion [2-7]. The use of polymeric material such as a conductor poly-pyrrole in the protection of metals is significantly reduce the rate of corrosion. This process it can be done by electro-polymerization, which can deposit polymer coatings on the substrate from a monomer-electrolyte solution. However, the aquatic electro-polymerization of pyrrole onto metals such as aluminum, steel and zinc has not been very effective because of the influence dissolution of these metals [8-10]. The zinc coatings to protective the high carbon steel (SWRH82B-1) which is using for bridge cable wires of high-strength steel, it was studied by Jing Hua Jiang et al. [11], to improve corrosion resistance. Sherardizing parameters were studied by the potentio-dynamic polarization, scanning electron microscopy, X-ray diffraction tests and optical microscopy. Another study shows that the addition of

Y2O3 activator for sherardizing coating, lead to slightly increases in the resistance of corrosion for sherardized of steel wire as compared with the addition of CeO2 powder [11]. Zhang and Zeng, they studied the corrosion behavior of the conductor polypyrrole coatings as a deposited layer on the (stainless steel-1Cr18Ni9Ti) by anodic polymerization from aquatic solutions of pyrrole and sodium dodecyl sulfate, and this investigated was done in the 0.3M of the aqueous solution of hydrochloric acid at room temperature by a combination of scanning electron microscopy and electrochemical measurement techniques, and after fifty-day of exposure, the experiments results indicated that the polypyrrole coating show the high stability, and high corrosion resistance [12]. Aim of this work corrosion protection of carbon steel. By two paint layers, the first layer using the sherardizing process, and the second layer using polypyrrole the conductor polymer.

2- Experimental Part

I. Material

Low carbon steel specimens were 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. Chemical analysis of pipeline material (low carbon steel) used in this search is shown in Table 1. Zinc powder with a purity of about 99.9%, whose chemical composition is shown in Table 2, which was used for coating.

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

Table 1: Chemical analysis of pipeline material (low carbon steel).

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

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%

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

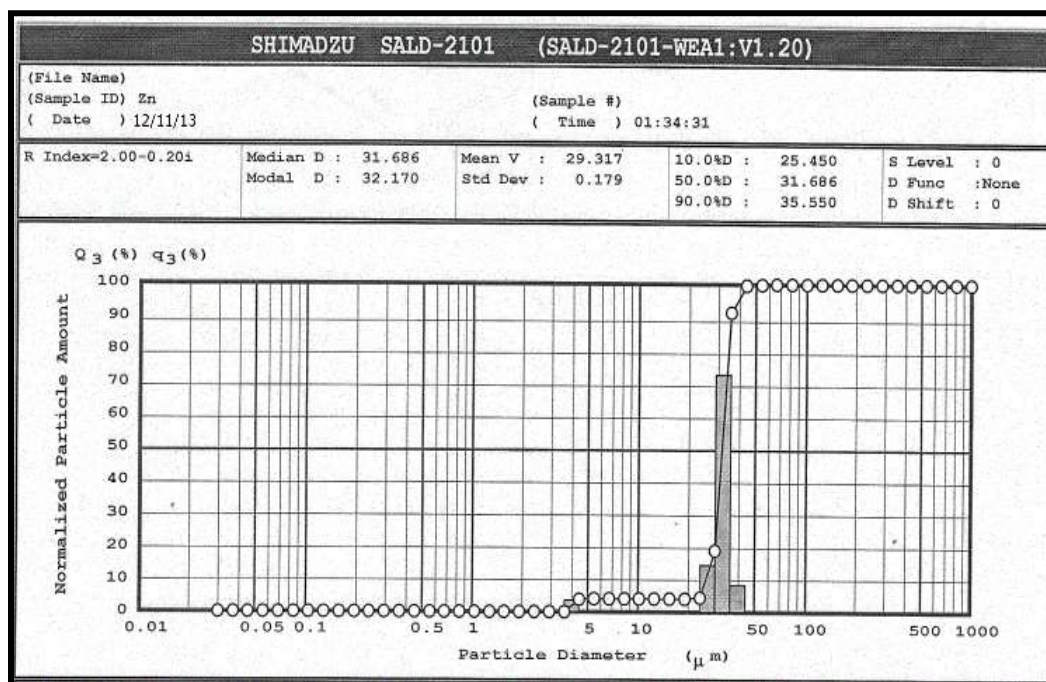


Figure 1: Particles size distribution of zinc powder

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 800°C for 2 hour) and to obtain clean surface, Then the samples are washed by water and equalled 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 800 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.

II. Sherardizing process

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

room temperature inside a switched off furnace.

III. Coating by conductor polymer (PPY)

This coating was done using pyrrole monomer; the electro-polymerization 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. Electro-polymerization was done in three electrodes system. A platinum electrode and a silver/silver chloride (Ag/AgCl) were used as counter and reference electrode respectively. The working electrode was made of carbon steel, polypyrrole (PPY) were electro-polymerized onto electrodes by cyclic voltammeter with a scan rate of 40mV/s. All the electro-polymerization reactions were carried out in the scan range of -100 to 2000 mV versus (Ag⁰/Ag⁺).

IV. Coating Thickness Measurement

The thickness of coating was measured after sherardizing processes by using automation machine, average of five readings were taken for each sample. Corrosion Test: To determine corrosion parameters (E_{corr} , i_{corr} and corrosion rate), the potentiostat instrument model (Wenking Mlab 200) Germany, was used in this work.

Microstructure test: to investigate the morphology of sherardized surface of low carbon steel and the surface of the various polymeric coatings, scanning electron microscope (SEM) model (TESCAN VEG-SB) made in Belgium was used.

3. Results and Discussion

I. Microstructure

The microstructure of the surface of low carbon steel before and after sherardizing coating are shown in Figures (2 a and b), Figure 2 (c and d), respectively shows that

the coating thickness at (15, 240 min) respectively. Microstructure characterization sherardizing of coating does not show a distinct crystal structure (unlike hot dip galvanizing where coating is formed initially by solidification from a melt) [3].

Coating thickness: The sherardizing coating thickness increases with treatment time as shown in Figure 3. The coating thickness increases from 21 μm 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

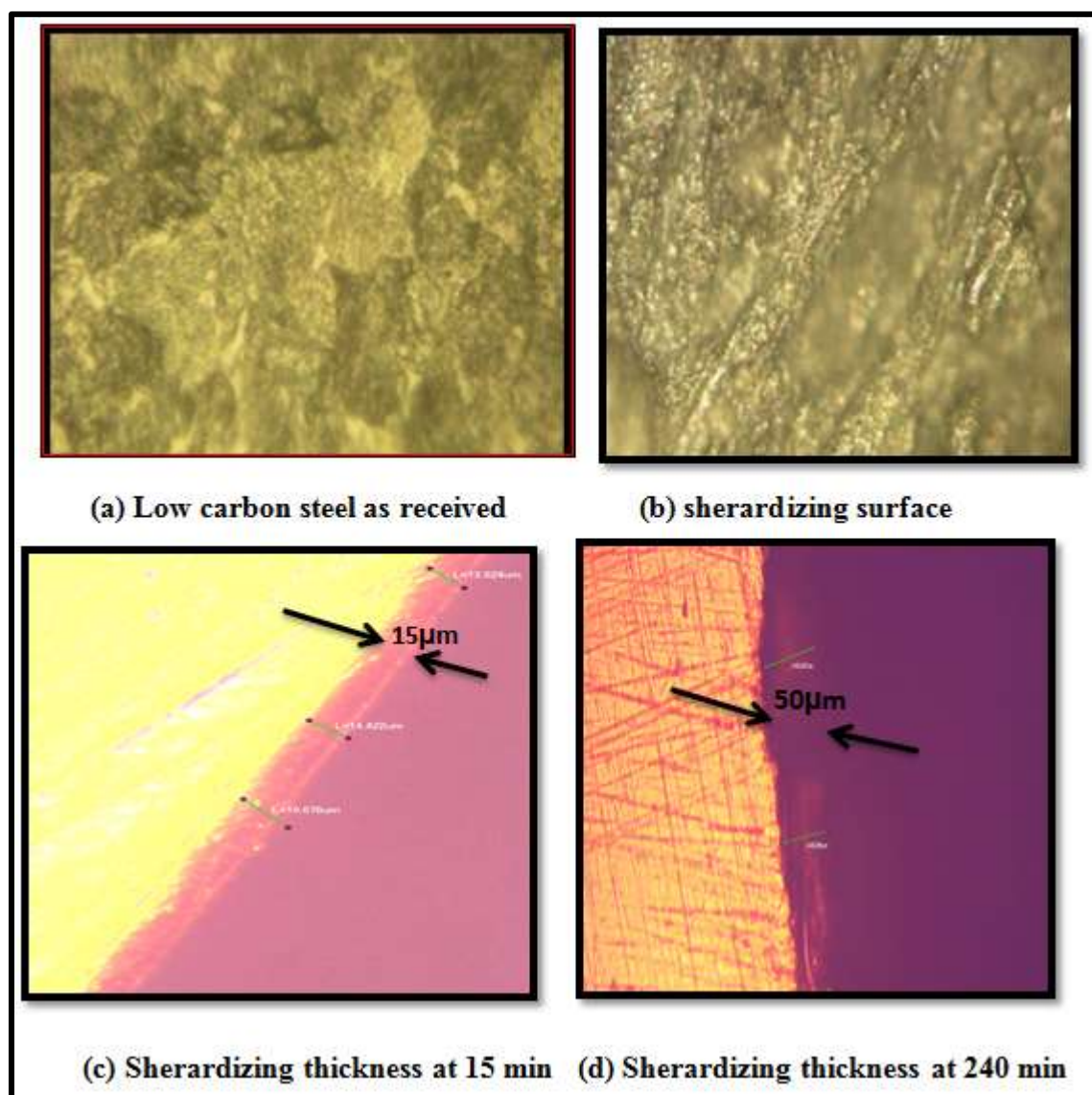


Figure 2: Optical micrographs of surface of (low carbon steel) samples before and after sherardizing coating.

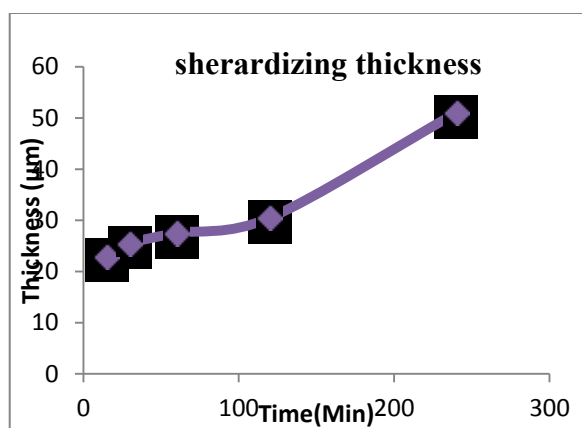


Figure 3: sherardizing thickness as a function of treatment time

II. Electrochemical Corrosion

To compares the corrosion resistance by using the polarization curves at pH=6.9 for the substrate as received (low carbon steel) Fig. 4 (a) with sherardizing coatings samples Fig. 4 (b, c, d, e and f), as well as with polymer conductive coatings specimens' Fig 5 (a & b). From these curves the values of electrochemical parameter (corrosion current density (i_{corr}) and corrosion potential (E_{corr})) for all samples at pH=6.9 was obtained and are listed in Tables (4) & (5), the kinetics of the corrosion reaction was evaluating by corrosion current density. The main difference between these curves is the corrosion current density and indicates that corrosion reactions take place at the interface, the higher corrosion potential means lower electrochemical activity and higher corrosion

resistance [13]. And it was reported that the samples of high thickness of sherardizing coating and with a microstructure of coating layer have lower porosity, that lead to an increase in corrosion resistance of the coated samples [14]. From Table 4 and Figure 4 it was found that the corrosion current density i_{corr} , for as received sample is $32.9 \mu A/cm^2$, 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 coating layer for the samples. From Fig. 5 and Table 5 it was observed that the corrosion current density i_{corr} , for the as received sample coated with polymer conductive (PPY) is $0.206 \mu A/cm^2$, while for the incorporation of sample with sherardized coat (at four hours) and PPY material reduces the corrosion rate to $0.107 \mu A/cm^2$.

The corrosion rate ((CR) (mil-inches per year)), was calculated from the corrosion current density ((i_{corr} ($\mu A.cm^{-2}$))) According to Faraday's Law [15]:

$$CR = 0.13 i_{corr} \frac{e}{\rho} \quad (1)$$

where:

ρ : Material density ($gm.cm^{-3}$).

e : Material equivalent weight (gm),

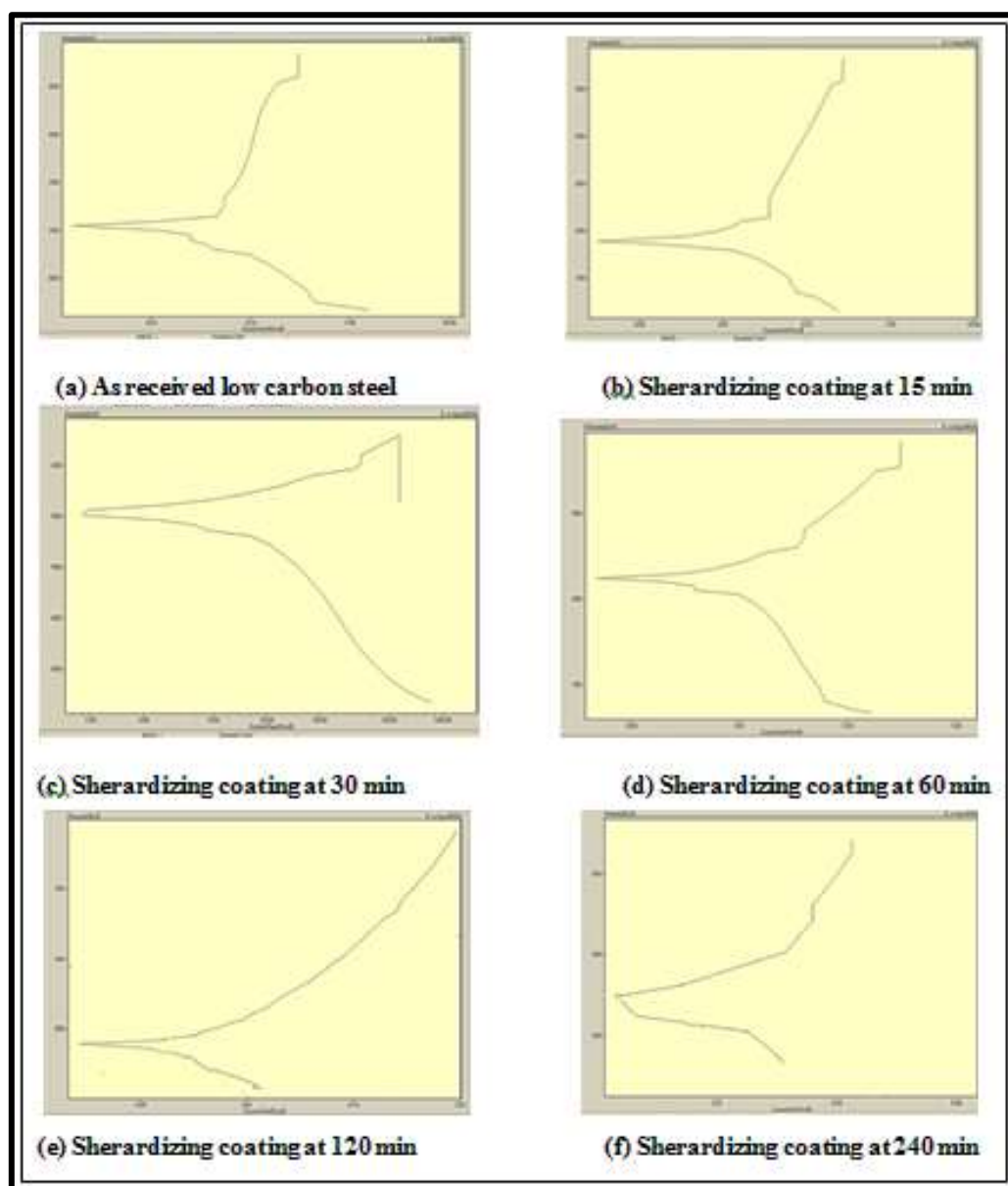
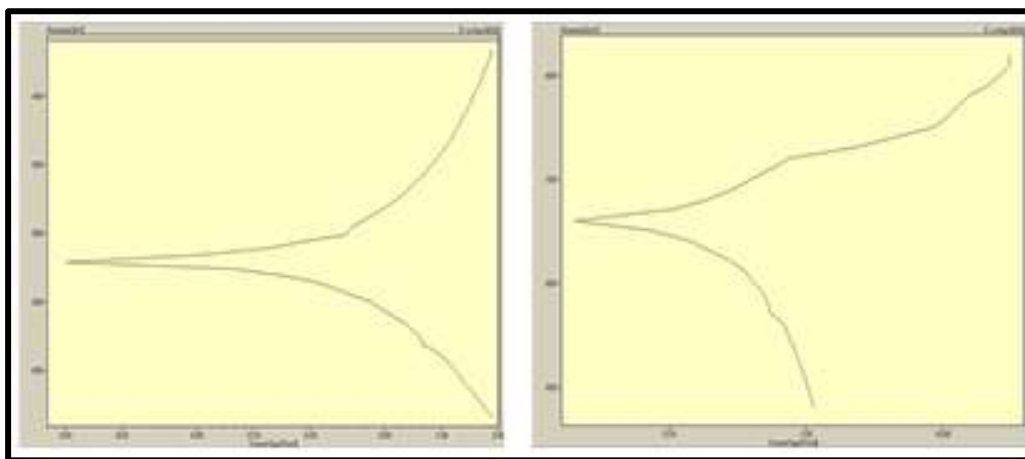


Figure 4: Potentiodynamic curves in NaCl for as received carbon steel and sherardizing steel at different coating thickness

Table 4: Corrosion parameters for coated steel carbon with sherardizing in 3.5 % NaCl,

Time coating	i_{corr} $\mu\text{A}/\text{cm}^2$	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



(a) PPY on steel (as received) (b) PPY on sherardizing coating
Figure 5: Potentiodynamic curves in NaCl for coated carbon steel.

Table 5: Corrosion parameter for coated steel carbon with sherardizing and polymer conductive

polymer conductive	i_{corr} $\mu A/cm^2$	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

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

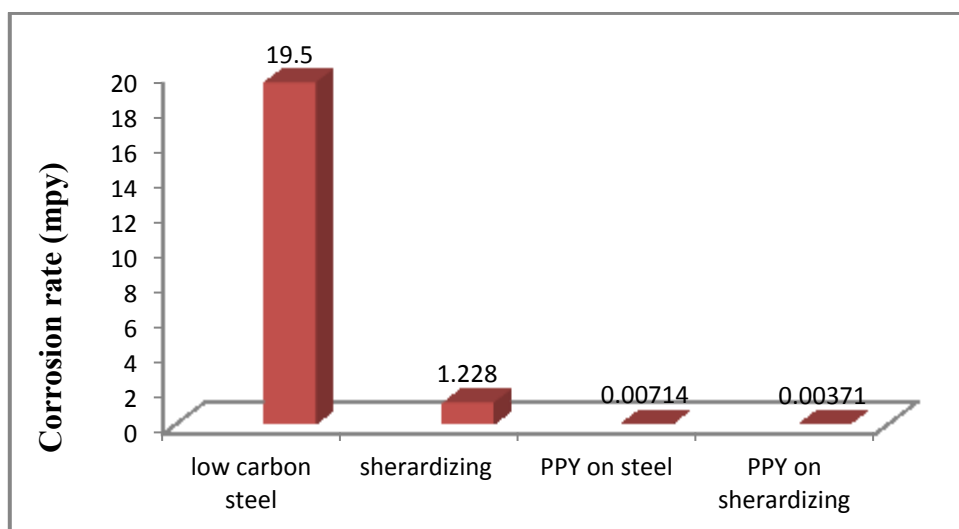


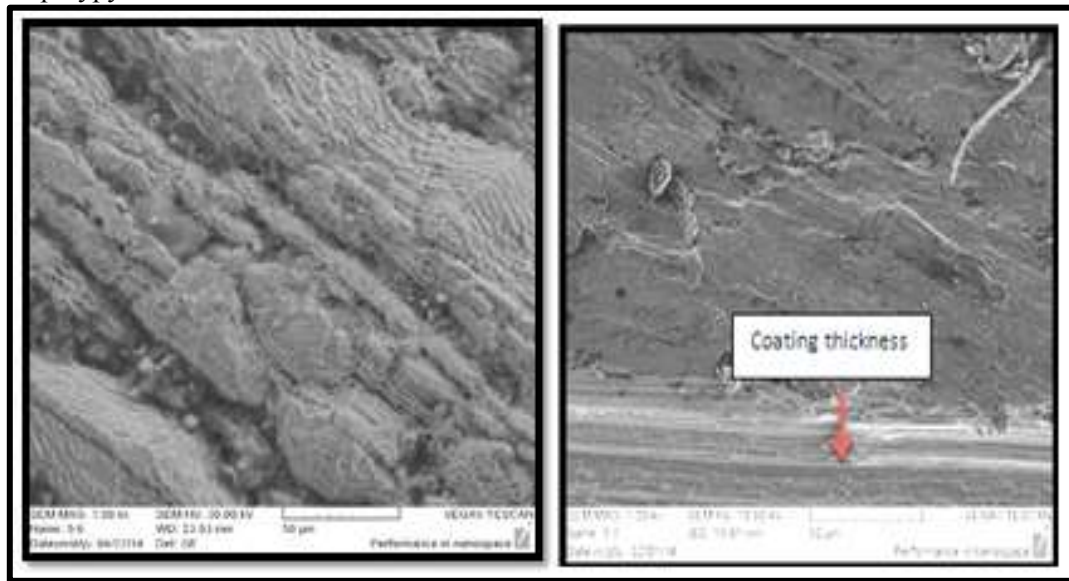
Figure 6: Corrosion rate at different coatings.

Morphology test: The surface morphology of the sherardizing coating, it is shown in Figure

7. It can be observed from Figure 7 (a), that the surface roughness for the sample coating by

sherardizing process, and was treated at 400°C for 4 hrs. is equal to 2.637 μm . And the Figure 7 b shows the thickness of sherardizing coating layer, for the same sample was equal to 51 μm . Figure 8. The image of scanning electron microscope, shows the different in the surface morphology of coated steel samples by sherardizing and polypyrrole the conductive polymer. The comparison of these micrographs images shows clearly, the difference in the surface morphology between polypyrrole conductive which were deposited over surface of low carbon steel bare (as received) Fig. 8 (c). and polypyrrole conductive which were

deposited over the sherardizing layer, which it was treated at 400°C for 4hrs, Fig. 8 (d), this shows formation of particles of polypyrrole material with interconnected network structure, it is noticed that the microstructure of the polypyrrole films is not smooth, have particles granular structure, the size of these granular structure in the range of (0.2-2) μm . as compared with polypyrrole conductive which were deposited over the surface of low carbon steel bare, the surface morphology for this have a larger size of granular structural (Fig. 8(c))



a) Surface morphology (surface roughness) b) thickness of sherardizing coating layer
Figure 7: Surface morphology of sherardizing coating layer, for the sample treated at 400°C for 4 hrs. (a) Surface morphology, shows the Surface roughness, and (b) thickness of sherardizing coating layer. (At the magnifications 1000 X)

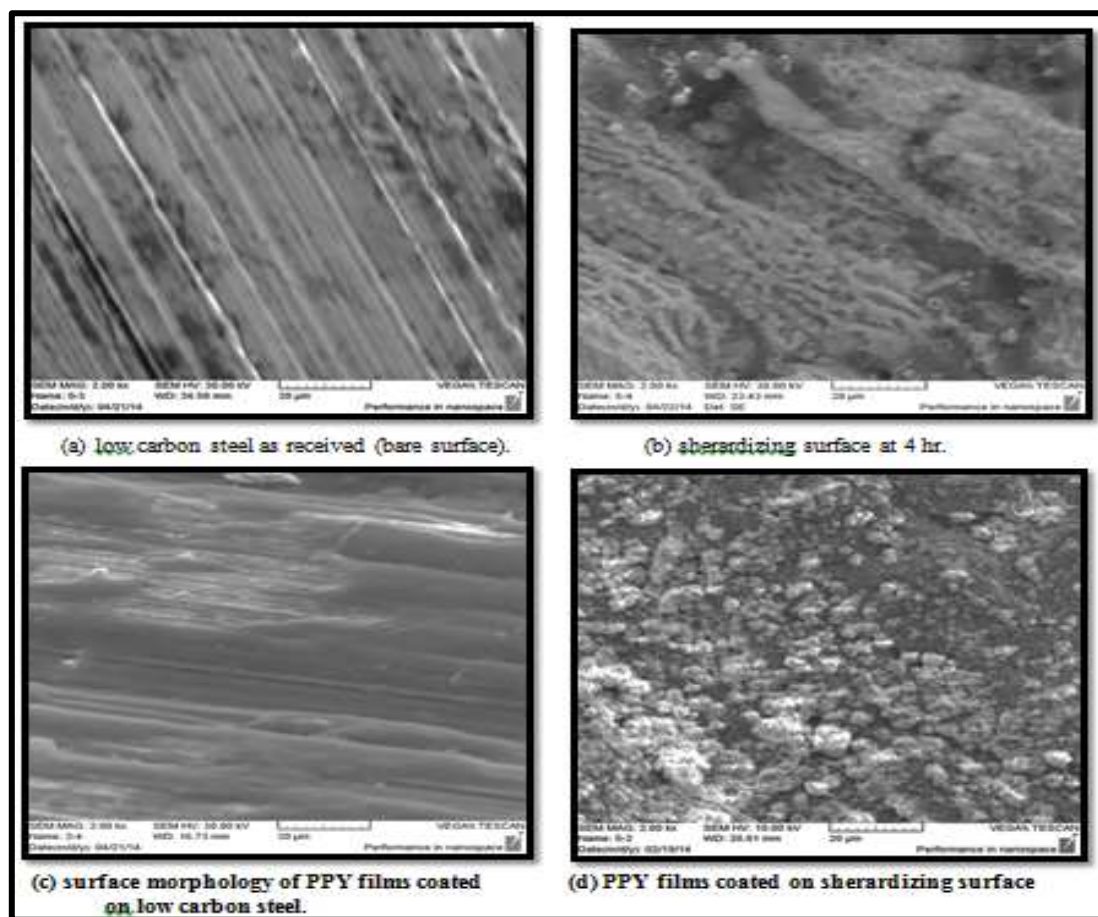


Figure 8: SEM of surface morphology for: (a) low carbon steel as received (bare surface), (b) sherardizing surface at 4 hr for low carbon steel, (c) polypyrrole films deposited on as received low carbon steel and (d) polypyrrole films deposited on sherardizing coating. (At the magnifications 2000X).

4. Conclusions

An attempt to protect oil pipelines and reservoirs from corrosion. The low carbon steel (oil pipelines) were coated by using two layers from different materials, the first layer was coating by sherardizing process, the second layer were coating by using polypyrrole the conductive polymer. And the following conclusions were obtained:

1. 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.
2. The corrosion current density (i_{corr}) and corrosion rate values are (32.9 $\mu\text{A}/\text{cm}^2$) and (19.5mpy) respectively, for as received sample (bare surface), whereas the incorporation of sherardizing coat for 15 min reduces (i_{corr}) to 15.44 $\mu\text{A}/\text{cm}^2$ and corrosion rate to 9.16 mpy, increasing the sherardizing treatment time to 4hrs decreased the i_{corr} to 2.07 $\mu\text{A}/\text{cm}^2$ and corrosion rate to 1.228 mpy. This means that coating the sample by sherardizing has improved the low carbon steel corrosion resistance.

3. Coating oil pipelines (as received) with bare surface by using polypyrrole the conductive polymer (PPY), lowered the i_{corr} and corrosion rate values to (0.2064 $\mu\text{A}/\text{cm}^2$ and 0.00714 mpy) respectively, which are much smaller as compared to low carbon steel and sherardizing coating samples.

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

5. Finally, based on what they offer. The coating of oil pipelines and reservoirs using consecutive two layers of sherardizing and conductive polymer. Raising the corrosion resistance to the high degree.

References

[1] J.R. Davis, Associates," Corrosion: Understanding the Basics", the Effects and Economic Impact of Corrosion, P: 237, 2000.

- [2] R.P. Edavan" R. Kopinski, "Corrosion resistance of painted zinc alloy coated steels" , V: 51, Issue 10, P: 2429–2442, 2009.
- [3] M. Moked and P. Eng, "Thermal Diffusion Galvanizing or TDG", A Cost Effective, Environmentally Friendly Process, 2006.
- [4] J. Kuhn, P. Labrenz, E. Bischoff, "Zinc coatings for hot sheet metal forming: Comparison of phase evolution and microstructure during heat treatment", Surface & Coatings Technology, 2012.
- [5] D. Kopyciński," The shaping of zinc coating on surface steels and ductile iron casting", Archives of Foundry Engineering, ISSN (1897-3310),V: 10 ,P: 463-468, 2010.
- [6] A. Bradley,"Corrosion Resistance of Electric Wire Terminals Used in Harsh Industrial Environments", White Paper, P:3-22, 2009.
- [7] Ji Hoon Park, Tea Ho Yun , Kyoo Young Kim , Yon Kyun Song and Jong Myung Park," The improvement of anticorrosion properties of zinc-rich organic coating by incorporating surface-modified zinc particle" , V: 74, Issue 1, P :25–35, 2012.
- [8] G.A. Snook, G.Z. Chen, D.J. Fray, M. Hughes, and M. Shaffer, "Studies of deposition of and charge storage in polypyrrole-chloride and polypyrrole-carbon nanotube composites with an electrochemical quartz crystal microbalance", J. Electroanal. Chem., 568, P: 135–142, 2004.
- [9] H. S. Abdulla and A. I. Abbo," Optical and Electrical Properties of Thin Films of Polyaniline and Polypyrrole", Int. J. Electrochem. Sci., 7 10666 – 10678, P: 1-13, 2012.
- [10] Gómez L. M., Olayo M. G., Cruz G. J., López-Gracia O. G., González-Torres M., "Effect of energy in the size of pyrrole-derived particles synthesized by plasma", Superficies by Vacío 25(2), P: 88-91, 2012.
- [11] Jing Hua Jiang, Ai Bin Ma, Xin Du Fan, Ming Zi Gong, Liu Yan Zhang, "Sherardizing and Characteristic of Zinc Protective Coating on High-Strength Steel Bridge Cable Wires", Periodical Advanced Materials-Research, V: 97–101,P: 1368-1372, DIO:10.4028/AMR.97 101.1368, 2010.
- [12] T. Zhang and C.L. Zeng," Corrosion protection of 1Cr18Ni9Ti stainless steel by polypyrrole coatings in HCl aqueous solution", Electrochimica Acta 50, P: 4721–4727, 2005.
- [13] LI De-zhi , HE Ye-dong ,WANG De-ren , ZHANG Zhao-en, QI Hui-bin ,GAO Wei ," Corrosion- erosion resistance of Zir Al co-cementation coatings on carbon steels in aqueous media", Trans .Nonferrous Met. Soc. Chine, V: 12, 2002
- [14] B.M. Durodola, J.A.O. Olugbuyiro, S.A. Moshood, O.S. Fayomi," Study of Influence of Zinc Plated Mild Steel Deterioration in Seawater Environment ", Int. J. Electrochem. Sci., 6, P: 5605 – 5616, 2011.
- [15] S.N. Popova, B. N. Popov and R.E. White, "Corrosion", V: 46, P: 1007, 1990.