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EFFECT OF CURRENT DENSITY AND DEPOSITON TIME ON GALVANOSTATIC PHOSPHATING OF LOW CARBON STEEL

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In this study, coating of zinc phosphate is applied by electrochemical method on low carbon steel substrates. Anodic current was used as an accelerator for the phosphating process. The effect of deposition time and current density on corrosion resistance was studied. For this purpose, analysis such as Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization measurements were carried out. Results indicated that lower current density and higher deposition time results in high quality coating i.e. good corrosion resistance. The protection mechanism offered by phosphate coating is discussed.

Keywords: Zinc Phosphate coating, Electrochemical Phosphating, Low carbon steel

1. Introduction

Metals which are extracted from their ores by chemical or electrochemical means show a strong tendency to revert to their oxide form at the first available opportunity, i.e., they tend to corrode. Corrosion can be defined as the destruction or deterioration of a material because of reaction with its environment [1]. So protection against corrosion is a need of time. Phosphating is widely used pre-treatment process for surface treatment and finishing of ferrous and nonferrous metals. Initially the process was developed as a simple method for corrosion protection but the end use of phosphated articles forced the modification of existing processes and development of innovative methods to substitute the conventional one [2]. Electricity serves as an accelerator in electrochemical method and use of chemical accelerators could be avoided making the process more eco-friendly [3]. Electrochemical method has shown good corrosion resistance than chemical methods and it is possible to carry out phosphating at room temperature by electrochemical phosphating [4, 5, 6]. Insulating and porous

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nature of coating provides the protection against corrosion [7]. In this work, therefore, zinc phosphate coating were applied on low carbon steel samples by anodic electrochemical method in phosphate bath and effect of current density and deposition time were investigated.

2. Experimental Procedure

Zinc phosphating bath contains zinc oxide, which is source of zinc, orthophosphoric acid and sodium hydroxide. Since the present study focuses on deposition of zinc phosphate coating on low carbon steel substrates by anodic electrochemical method no additives were added in the electrolyte solution. Only basic constituents were used. Chemical composition of electrolyte solution is given in Table 1. pH of bath was 3.2. Low carbon steel (AISI 1015) substrates of 80 mm x 20 mm x 0.25 mm in size were used, out of which 50 mm x 20 mm x 0.25 mm area was exposed for deposition of coating by anodic phosphating process. The oil and greasy matter present on substrate material were removed by wiping with cotton soaked in Trichloroethylene. These degreased panels were pickled in 10% sulphuric acid at 70-80 ^{0}C for 4-6 min to remove rust and scale. The pickled samples were cleaned by distilled water to remove acid residues present on it after pickling. These substrates were then immersed into phosphating solution in a beaker, which is at room temperature. Two graphite rod electrodes were placed on the both sides of low carbon steel electrodes. The deposition of the zinc phosphate coating was carried out under galvanostatic conditions using a Gamry Interface System 1000. Process variables are shown in Table 1.

Table 1

Chemical composition and process parameters

Chemicals	Quantity
ZnO	2.04 g
H_3PO_4	16 ml
NaOH	6.67g
Process variables	
Current Density	2, 4, 6, 8 and 10 mA/cm^2
Deposition Time	20, 40 and 60 min.

Potential – Time measurement during anodic phosphating was carried out. After completion of deposition process sample is cleaned by demineralized water and then dried in hot air stream. The corrosion resistance of samples in 3.5% sodium chloride solution is carried out with the help of Electrochemical Impedance Spectroscopy and Tafel polarization methods. A corrosion cell having three electrode geometry consisting of the coated sample having area 8 cm ^{2} as working electrode, platinum as counter electrode and saturated calomel electrode as a reference electrode was used. The cell was coupled with the Gamry reference system 600, USA for electrochemical studies. .Potentiostatic impedance spectroscopy in the frequency range from 100KHz to 0.01 Hz with an initial delay of 1800 sec and 10 mV votage was employed. All measurements were carried out five times to obtain good reproducibility of the results. Tafel plots were generated by scanning from corrosion potential to 250 mV in both – anodic and cathodic directions. Exact amount of zinc phosphate deposited on the substrate was calculated by dipping the samples for 5 min into a solution containing 4% triethanolamine (TEA), 12% di-sodium salt of ethylene diamine tetra-acetic acid (Na_2EDTA), 9% NaOH and distilled water.Optimized coating thickess was 10 microns.

3. Results and discussion

3.1 Potential-Time Measurement

During anodic phosphating, the potential of substrate is monitored continuously as a function of time. Fig. 1 shows a relation between potential and time during deposition,

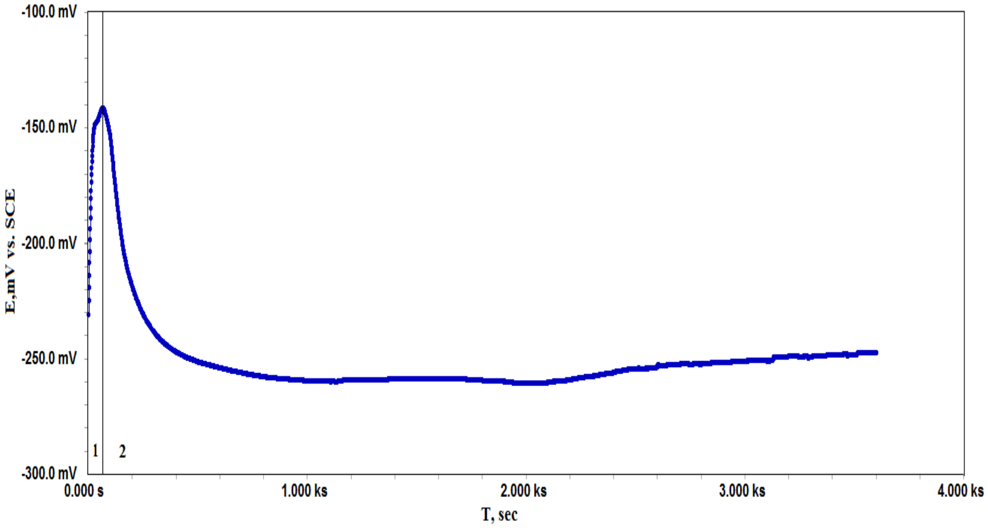

Fig. 1 Relation between Potential and Time during deposition, 1) Metal Dissolution 2) Phosphate Deposition

Fig 1 shows that potential initially shifted to anodic region (Region 1) and reached a maximum value. With further increase in time potential of substrate shifted towards cathodic region (Region 2). Anodic shift is due to depletion of H^+ ions in electrode/electrolyte interface caused by repulsive forces of ferrous ions and the positive charge on substrate. Maximum potential suggest the start of conversion of primary soluble phosphate into tertiary insoluble phosphate. Due to deposition of this non-metallic zinc phosphate coating potential of substrate shifts to cathodic region.

3.2 Effect of current density on coating weight

It is found that after dipping the sample into striping solution almost all coating is dissolved. Weight of phosphated substrates before and after dipping into EDTA based solution were noted. Fig 2 shows effect of current density on coating weight.

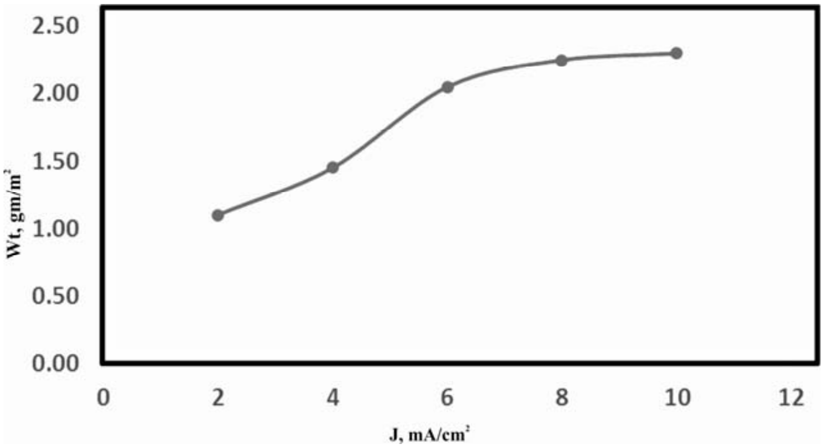

Fig 2. Effect of current density on coating weight

Fig 2 shows that with increasing the current density coating weight increased. As the current density increases the rate of hydrogen evolution reaction increases which alters the chemical equilibrium between primary soluble phosphates and tertiary non soluble phosphates. Due to this, early conversion of primary soluble phosphate into tertiary non soluble phosphate occurs. This leads into higher deposition of coating weight with increase in current density. After 8 mA/cm^2 coating weight reaches stable value and this because of spalling of coating at higher current density.

3.3 Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy study of phosphated samples at different deposition current density 2, 4, 6, 8 and 10 mA/cm^2 for 60 min of deposition time at 0 hours of immersion were carried out and it is used to estimate performance of coating from corrosion resistance point of view. Bode and Nyquist plots of Zinc phosphate coated sample at 2, 4, 6, 8 and 10 mA/cm^2 deposition current density at 60 min deposition time are shown in Fig 3 and 4.

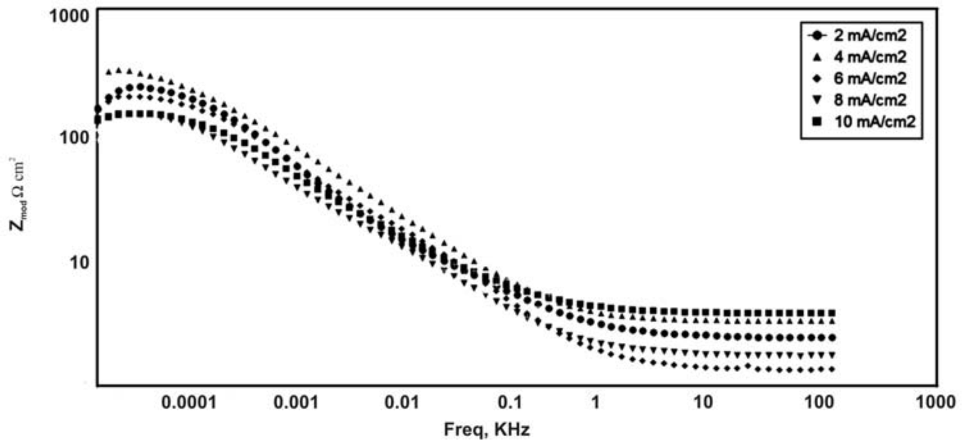

Fig 3. Bode plot of Zinc phosphate coated sample at 2, 4, 6, 8 & 10 mA/cm^2 for 60 min.

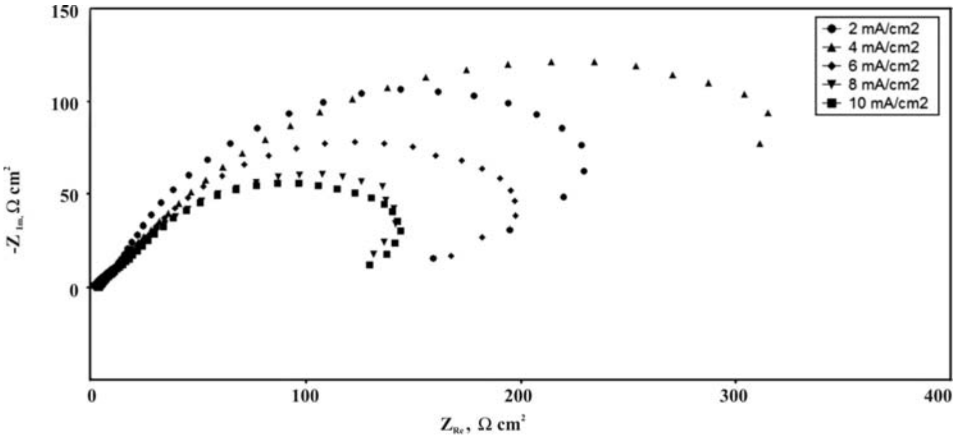

Fig 4. Nyquist plot of Zinc phosphate coated sample at 2, 4, 6, 8 & 10 mA/cm^2 – 60 min.

It is seen from Fig 3 that with increasing the deposition Current density impedance value (Z_{mod}) decreased. Fig 4 shows the capacitive loops with different diameters. As the deposition Current density increased the radius of the loops decreased. Fig. 5 shows equivalent circuit used for simulating impedance behaviour of coatings. EIS results for zinc phosphate coated steel samples at 4 mA/cm^2 – for 60 min are shown in Table 2.

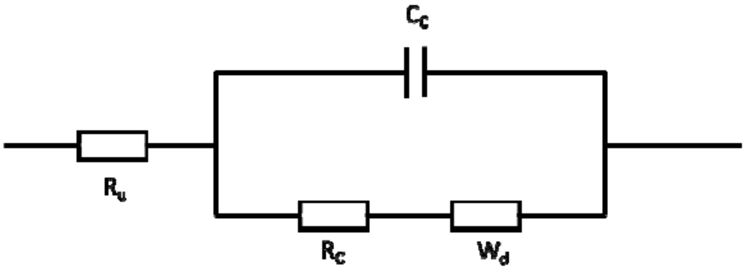

Fig. 5 Equivalent circuit used for simulating impedance behaviour of coatings

Table 2

EIS results for zinc phosphate coated steel samples at different current density

Sample No.	Deposition Current Density (mA/cm^2)	Coating Resistance R_c (Ω.cm^2)	Coating Capacitance C_c (F)	Warburg Constant W_d	Z_{mod} (Ω.cm^2)	Z_{real} (Ω.cm^2)
1	2	286.2	0.29	194.80	240.7	144.1
2	4	406.8	0.20	11.02	328.8	214.1
3	6	239.4	0.25	200.73	202.7	122.8
4	8	196.9	0.43	202.46	147.1	107.6
5	10	178.5	0.33	650.97	232.0	86.69

It is seen from Table 2 that as the deposition current density increased the coating resistance (R_c) increased from 286.2 Ω.cm^2 to 406.8 Ω.cm^2 initially. But further increase in deposition current density resulted into decreased coating resistance of coating. As the deposition current density increased the coating capacitance (C_c) decreased from 0.29 F to 0.20 F initially. But further increase in deposition current density resulted into increased coating capacitance (C_c) of coating. So from these results it can be predicted that as the deposition current density increases the porosity in coating increased and coating damaged easily. Out of all, sample with 4 mA/cm^2 deposition current density has shown the highest coating resistance and lowest coating capacitance so effect of deposition time on this coating is further evaluated. Electrochemical Impedance Spectroscopy study of phosphated samples at different deposition time 20, 40 and 60 for 4 mA/cm^2 deposition current density at 0 hours of immersion were carried out. Bode and Nyquist plots of Zinc phosphate coated sample at 4 mA/cm^2 deposition current density at different deposition time are shown in Fig 6 and 7.

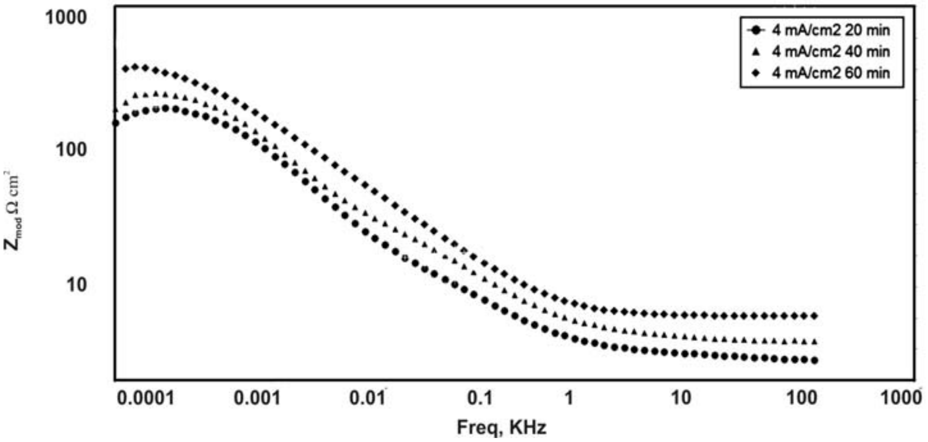

Fig 6. Bode plot of zinc phosphate coated sample at 4 mA/cm^2 - 20, 40 and 60 min.

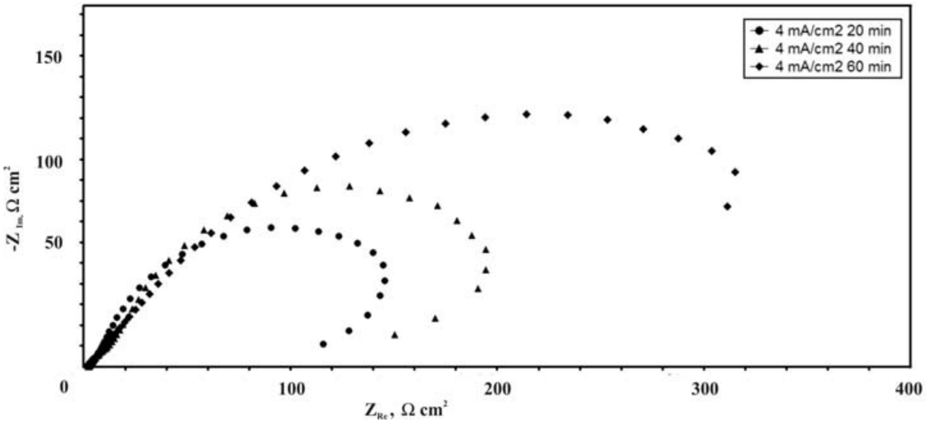

Fig 7. Nyquist plot of zinc phosphate coated sample at 4 mA/cm^2 - 20, 40 and 60 min.

It is seen from Fig 6 that with increasing the deposition time impedance value (Z_{mod}) increased. Fig 7 shows the capacitive loops with different diameters. As the deposition time increased the radius of the loops decreased. EIS results for zinc phosphate coated steel samples at 4 mA/cm^2 - 20, 40 and 60 min are showed in Table 3. It is found that as deposition time increased from 20 to 40 min coating resistance increased from 184 Ω.cm^2 to 255.5 Ω.cm^2. It suggest that increasing deposition time increased the coating thickness and this helped in increasing the coating resistance. Coating resistance is further improved from 255.5 Ω.cm^2 to 406.8 Ω.cm^2 with increasing the deposition time from 40 to 60 min. It is found that as deposition time increased from 20 to 40 min coating capacitance decreased from 0.40 F to 0.33 F.

Table 3

EIS results for zinc phosphate coated steel samples at 4 mA/cm^2 - 20, 40 and 60 min

Deposition Time (min)	Current Density (mA/cm^2)	Coating Resistance R_c (Ω.cm^2)	Coating Capacitance C_c (F)	Warburg Constant W_d	Z_{mod} (Ω.cm^2)	Z_{real} (Ω.cm^2)
20	4	184	0.40	274.69	152.7	90.63
40	4	255.5	0.33	212.44	202.7	128.5
60	4	406.8	0.20	11.01	328.8	214.1

It suggests that increasing deposition time, the coating thickness increased with decreasing the porosity and this resulted into decreased the coating capacitance. Coating capacitance is further decreased from 0.33 F to 0.20 F with increasing the deposition time from 40 to 60 min. So the increasing value of coating resistance and decreasing value of coating capacitance suggest improvement in coating quality with increasing deposition time.

3.4 Potentiodynamic Polarization Study

Potentiodynamic polarization study of phosphated samples at different deposition current density 2, 4, 6, 8 and 10 mA/cm^2 for 60 min of deposition time were carried out. Also same study is carried out for uncoated steel.

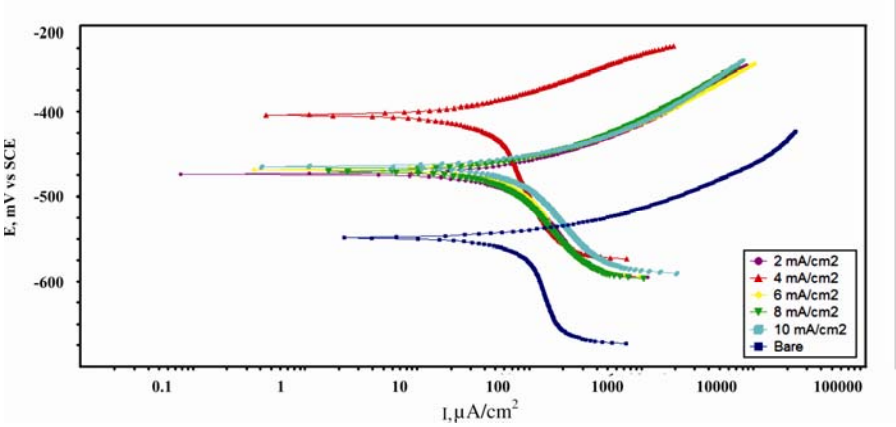

Fig 8. Tafel plot for phosphated low carbon steel sample at 2, 4, 6, 8 and 10 mA/cm^2 -60 min in 3.5 wt % NaCl

The values of corrosion current density, corrosion potential, and corrosion rates obtained from Fig. 8 are recorded in Table 4.

Table 4

Corrosion current density, corrosion potential and corrosion rates of bare steel and phosphated steel samples

Sample No.	Deposition Current Density (mA/cm^2)	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	Corrosion Rate (mpy)
Uncoated	-	81.3	-697.0	9.19
Phosphate coated	2	78.40	-548.0	4.48
Phosphate coated	4	40.90	-408.0	2.33
Phosphate coated	6	83.90	-537.0	4.79
Phosphate coated	8	87.40	-542.0	4.99
Phosphate coated	10	94.30	-530.0	5.38

Corrosion potential is found to be decreased from -697.0 mV for bare steel to -548 mV for phosphated samples at 2 mA/cm^2 deposition current density. Compared to bare steel, corrosion potential of all phosphated samples is shifted to cathodic region. It should also be noted that the corrosion rate is reduced due to decrease in current density from 81.3 $\mu A/cm^2$ to 78.40 $\mu A/cm^2$ for bare steel, phosphated steel at 2 mA/cm^2 deposition current density respectively. Corrosion rate for bare steel in 3.5 % NaCl solution is found to be 9.19 mpy whereas lowest corrosion rate for phosphated sample at 4 mA/cm^2 deposition current density is found to be 2.33 mpy. It should also be noted that as the phosphate deposition current density increases corrosion current density decreased initially from 78.40 $\mu A/cm^2$ to 40.90 $\mu A/cm^2$ which resulted in decreased corrosion rate from 4.48 to 2.33 mpy. It should also be noted that as deposition current density increased further corrosion current density increased and resulted in increased corrosion rate. Table 4 shows that out of all phosphated samples at different deposition current densities sample with 4 mA/cm^2 current density shows the minimum corrosion rate. So the effect of deposition time on corrosion rate is further studied on the sample with 4 mA/cm^2 current density. Potentiodynamic polarization study of phosphated samples at different deposition time 20, 40 and 60 min for 4 mA/cm^2 deposition current density were carried out. Potentiodynamic Polarization behaviour of zinc phosphated sample at 4 mA/cm^2 deposition current density for 20 min in 3.5 wt. % NaCl solution is depicted in Fig 9.

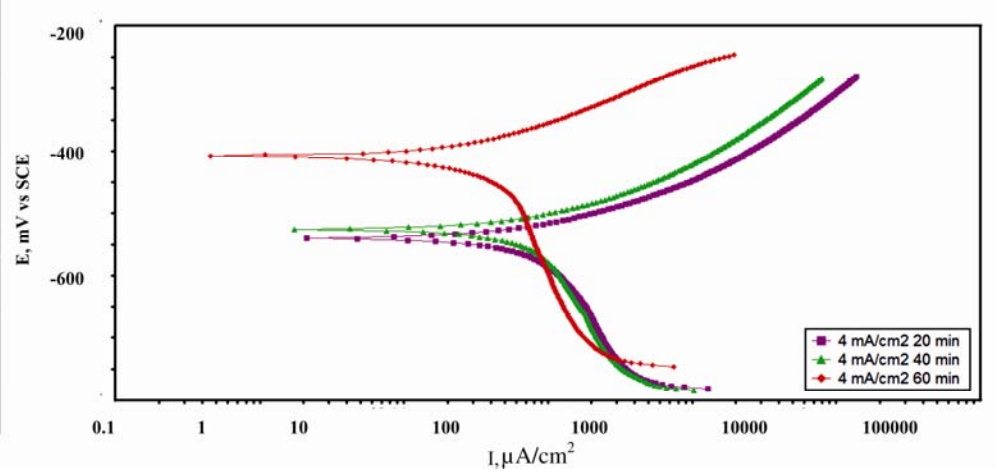

Fig 9. Tafel plot for phosphated steel samples at 4 mA/cm^2 20, 40 and 60 min in 3.5 wt % NaCl

The values of corrosion current density, corrosion potential, and corrosion rates obtained from Fig. 9 are recorded in Table 5
Corrosion potential is found to be decreased from -540 mV for 20 min deposited to -525 mV for 40 min phosphated samples at 4 mA/cm^2 deposition current density. It is noted that with further increase in deposition time the corrosion rate decreased. Corrosion rate is reduced due to decrease in current density from 156.96 µA/cm^2 to 40.90 µA/cm^2 for 20 min, 60 min phosphated steel at 4 mA/cm^2 deposition current density respectively. Corrosion rate for 20 min phosphated sample in 3.5 % NaCl solution is found to be 8.98 mpy whereas corrosion rate for 60 min phosphated sample at 4 mA/cm^2 deposition current density is found to be 2.33 mpy.

Table 5

Corrosion current density, corrosion potential and corrosion rates of phosphated steel samples

Deposition Time (min)	Deposition Current Density (mA/cm^2)	I_{corr} (µA/cm^2)	E_{corr} (mV)	Corrosion Rate (mpy)
20	4	156.96	-540.0	8.98
40	4	142.96	-525.0	8.17
60	4	40.90	-408.0	2.33

Table 5 shows that out of all phosphated samples at different deposition time, sample with 60 min deposition shows the minimum corrosion rate. So sample with 60 min deposition time and 4 mA/cm^2 current density has shown highest corrosion resistance.

3.5 Protection mechanism of Phosphate Coating

The insulating property of phosphate coating provides an important contribution to preventing the corrosion of steel substrate. Being insulating nature phosphate coating does not take part in any electrochemical reaction. In a corrosion process steel substrate solution and interface creates an electric circuit between anode and cathode. The corrosion rate depends on total resistivity of circuit. Compared to an electrically conducting coating, phosphate coatings increase the circuit resistivity. The electric transportation processes during the corrosion is hindered. As the anodic and cathodic processes can only continue at the bottom of pores within the coating, the transportation of reactant and corrosion product through the coating is also obstructed. At lower current density the porosity in the coating is less. Due to this corrosion rates were decreased at low current density.

4. Conclusions

It is possible to obtain zinc phosphate coating on low carbon steel samples using anodic electrochemical deposition technique. With increasing the current density, weight of the coating gets increased. Coating resistance with 4 mA/cm^2 deposition current density decreased from 406.8 Ω.cm^2 to 178.52 Ω.cm^2 for sample with 10 mA/cm^2 deposition current density. This reveals that with increasing the deposition current density the corrosion resistance of coating gets decreased. Coating capacitance of coating increased from 0.20 F to 0.33 F for sample with 4 mA/cm^2 and 10 mA/cm^2 deposition current density respectively.

Coating resistance increased from 184 Ω.cm^2 to 406.8 Ω.cm^2 for sample with 4 mA/cm^2 deposition current density with 20 min and 60 min deposition time respectively. This reveals that with increasing the deposition time the quality of coating increased. Coating capacitance of coating decreased from 0.40 F to 0.20 F for sample with 4 mA/cm^2 deposition current density with 20 min and 60 min deposition time respectively. The corrosion rate of zinc phosphate coated low carbon steel in 3.5 wt. % NaCl is found to be 2.33 mpy which is about 4 times lower than that of uncoated low carbon steel in the same solution.

Lowest corrosion rate is 2.33 mpy with 4 mA/cm^2 current density and 60 min deposition time. This suggest that these are the optimum values of process variables for anodic phosphating by electrochemical method. Phosphate coatings being insulating in nature does not take part in any electrochemical reaction, as the anodic and cathodic processes can only continue at the bottom of pores within the coating, the transportation of reactant and corrosion product through the coating is also obstructed.

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