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Research Article

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Nano-TiO$_2$ Phosphate Conversion Coatings – A Chemical Approach

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Abstract: The present study aims at deposition of zinc phosphate coatings on low carbon steel with incorporated nano- TiO$_2$ particles by chemical phosphating method. The coated low carbon steel samples were assessed in corrosion studies using electrochemical impedance spectroscopy and potentiodynamic polarization techniques (Tafel) in 3.5% NaCl solution. Morphology and chemical composition of the coatings were analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy in order to observe growth of coating. Significant variations in the coating weight, porosity and corrosion resistance were observed with the addition of nano-TiO$_2$ in the phosphating bath. Corrosion rate of nano-TiO$_2$ chemical phosphate coated samples was found to be 3.5 milli inches per year which was 3 times less than the normal phosphate-coated sample (8 mpy). Electrochemical impedance spectroscopy studies reveal reduction of porosity of nano-TiO$_2$ phosphate coated samples. It was found that nano-TiO$_2$ particles in the phosphating solution yielded uniform phosphate coatings of higher coating weight, fewer defects and enhanced corrosion resistance than the normal zinc phosphate coatings (developed using normal phosphating bath).

Keywords: Chemical phosphate coatings, EIS, Nano-TiO$_2$, Tafel

1 Introduction

Metals are thermodynamically unstable in their refined environment and they have a propensity to revert back to their original state, they are prone to corrode. Corrosion is the common destruction of material experienced when it reacts with its environment [1]. Corrosion being the loss of energy can be encountered by using conversion coating, sacrificial anodes and by the use of some conducting polymer coatings [2]. There is a growing need to prevent metals from the attack of corrosion. In current scenario, development of self-healing coatings is boosting the engineering community to prevent the base metal from corrosion [3].

Phosphate coating being insoluble by nature is the common and efficient industrial pretreatment process and can be deposited by two methods: chemical and electrochemical [4]. Phosphate coatings have other specific features in context of corrosion protection. Phosphate coatings can afford excellent corrosion resistance with optimal speed of operation and have better adhesion. Though the process was initially developed as a simple method for prevention of corrosion, the changing end use of phosphate coated products forced the modification of existing processes and development of innovative methods to substitute the conventional ones.

Few relevant studies about the effects of incorporation of nano-metal dioxides and corrosion protection ability of phosphate coatings have yet been reported. One platform, by adding the nano-TiO$_2$ in phosphating bath with zinc oxide, was investigated [5]. However, low temperature phosphating processes are very slow and need to be accelerated by some means. Acceleration of the phosphating process could be achieved by chemical, mechanical and electrochemical methods. However, each of them has some limitations and/or detrimental effects. Chemical accelerators are the preferred choice in many instances [7]. It should be stressed that, while phosphate coatings always affect corrosion protection, its effects are not always necessarily positive.

Therefore in present study, zinc phosphate coatings are developed by incorporating nano-TiO$_2$ particles in the phosphating bath by chemical method. The coated

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samples are tested by potentiodynamic polarization studies in order to assess corrosion protection performance; these were supported by electrochemical impedance spectroscopy (EIS). Though the coatings are made by chemical phosphating method, for corrosion studies only electrochemical aspects were studied. Comparative studies are made with bare uncoated, normal phosphate coated and nano-TiO_2 phosphate coated samples.

2 Materials and Experimental

Low carbon steel substrates (AISI 1015) of 8 cm × 2 cm × 0.4 mm size were used as the substrate material for the deposition of zinc phosphate coating by chemical method. Dust particles, oil, greasy matter present on the substrate which would inhibit coating formation were removed by cleaning with acetone. A standard phosphating bath (SURFIX ZN 603) was used for the zinc phosphate deposition. Nano-titanium dioxide powder (particle size 21 nm) used for incorporation in the phosphating bath was imported from the supplier (Aldrich Chemicals Pvt. Ltd.). Synthesis and characterization of nano-TiO_2 powder was performed in order to scale up the properties of nano-TiO_2 powder. The XRD patterns of nano-TiO_2 were obtained using X-ray diffractometer with CuK_α radiation in the range of 20-70^0 (λ= 0.15418 nm). UV-Vis absorption spectra of nano-TiO_2 were recorded using 5E spectrophotometer at room temperature in the range of 200 to 700 nm. The deposition bath containing phosphate solution was prepared by adding nano-titanium dioxide powder (~ 21 nm) and heating up to 70°C. The substrates were dipped in the phosphating bath for 5 minutes. The phosphate coated samples were rinsed with deionized water to remove the acid and the soluble salts left after phosphating. After rinsing, the specimens were dried using an air dryer. The surface morphology and chemical composition of the nano-TiO_2 phosphate coatings were further studied using scanning electron microscopy and energy dispersive X-ray spectroscopy EDX respectively. The purpose of carrying out the EDX is to confirm the presence of nano-titanium dioxide in the coatings. Potentiodynamic polarization studies were carried out using a potentiostat (GAMRY Instrument Interface 1000) at the open circuit potential. The zinc phosphate-coated low carbon steel substrates were used as the working electrode, whereas saturated calomel electrode (SCE) and a platinum electrode served as the reference and counter electrode respectively. Gamry Echem Analyst software was used for data acquisition and analysis. Polarization measurement was carried out from initial potential of - 0.25 V to the final potential of 0.25 V with respect to open circuit potential. Electrochemical impedance studies were carried out at open circuit potential in the frequency range between 100000 and 0.01 Hz. The corrosion potential and corrosion current density were determined using Tafel extrapolation method. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from Nyquist plot by fitting the data using Gamry software.

3 Results and Discussion

Synthesis and Characterization of nano-TiO_2 powder

Ultrafine TiO_2 particles have been synthesized by a sol gel method by the supplier and successfully characterized by XRD and UV-Vis spectroscopy. The XRD patterns of TiO_2 are shown in Figure 1. The nano-particles show crystalline nature with 2θ peaks at 2θ = 25.56 (101), 2θ = 38.15 (004), 2θ = 49.05 (200), 2θ = 54.45 (105), 2θ = 63.36 (204), 2θ = 69.20 (220) and 2θ = 75.15 (215). A preferred orientation corresponding to (101) plane is observed. All peaks in the XRD patterns could be indexed to anatase phase of TiO_2 and diffraction data are in good agreement with JCPDS data [8]. Crystallite size was obtained by Debye-Scherrer's equation

$$D = K\lambda/(\beta cos\theta)$$

where D is the crystal size, λ is the wavelength (λ = 0.15418 nm) for $CuK\alpha$, K is usually taken as 0.89 and β is the line width at half maximum height [9]. Clear nanostructures were seen having grain sizes of ~ 25 nm which were in good agreement with the grain size suggested by supplier ~ 21 nm. UV-Vis absorption spectrum was obtained in order to characterize the optical absorbance of the nano-TiO_2 particles. The absorption spectrum of TiO_2 nano-particles is shown in Figure 2 with band edge at 378 nm. The optical band gap energy can be evaluated using following equation,

$$\alpha = \frac{K\,(h\upsilon - E_g)^n}{h\upsilon}$$

where α is the absorption coefficient, K is a constant, E_g is the band gap and n = 1 for direct transition. Here direct transition was assumed, as a counterpart there exist indirect (n = 2), forbidden direct (n = 1.5) and forbidden indirect (n = 3) transitions. An endeavor has been made in this section to understand the nature of nano-particles and their physical relevance in phosphate coatings. It was found that the band gap energy of nano-TiO_2 particles calculated from above equations is 3.58 eV which is larger

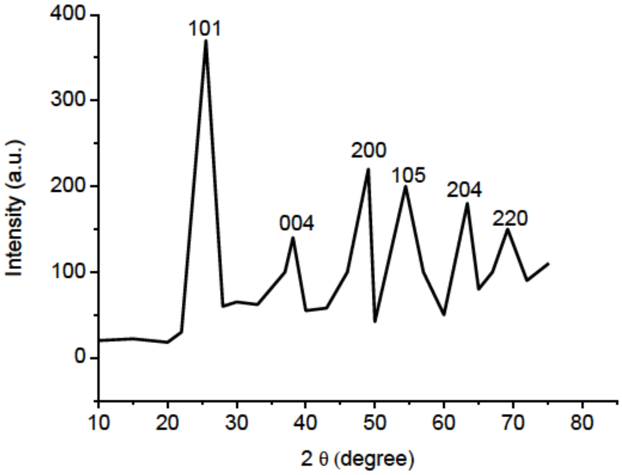

Figure 1: XRD pattern of TiO$_2$ nanoparticles.

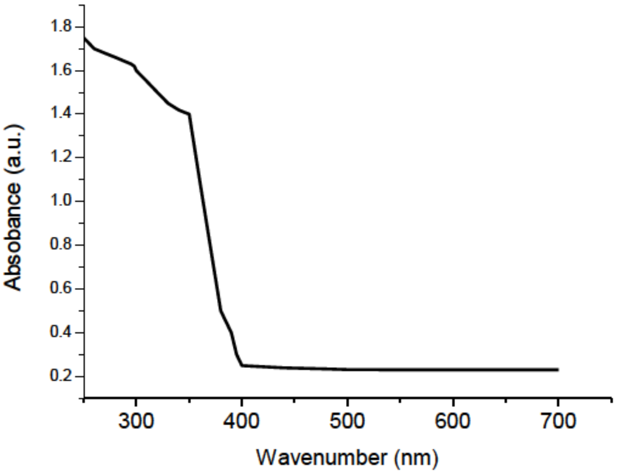

Figure 2: UV-visible absorption spectra of TiO$_2$ nanoparticles.

than for bulk nano-TiO$_2$ powder (3.46 eV), this could be attributed to the fact that band gap energies are particle size dependent. This current hypothesis is very much in line with observations made by Reddy [18]. It could be concluded that decrease in particle size subsequently affects the band gap (tend to increase). The current exercise accounts for significance of synthesis and characterization studies of nano-TiO$_2$ particles for validation of nano-particle size and could be attributed to the hypothesis as particles of smaller size should have larger band gaps (~21nm for 3.67 eV) (Figure 3).

Chemical Phosphate Deposition

During the initial experimental work, 2 g/L of nano-TiO$_2$ was used in the phosphating bath to investigate the effect of nano-TiO$_2$ on the coating weight, morphology, chemical composition, corrosion resistance and electrochemical impedance spectroscopy. It was observed that there is significant increase in the estimated coating weight due to the incorporation of nano-TiO$_2$ particles in the phosphating bath with an immersion time of 5 min at 70 °C °. The ASTM standard A754 was implemented for coating weight measurement and further details can be extracted from [19]. The increase in the coating weight and decrease in the metal dissolution can be attributed to the increased number of nucleation sites and reduction in the size of the crystal clusters of zinc phosphate deposited on the low carbon steel. The apparent gain in the weight of the samples before and after coating of phosphate provides a preliminary estimate of the amount of phosphate coated on them. It was observed that nano-TiO$_2$ phosphate coatings were heavier in comparison with the normal phosphate coating (Figure 4).

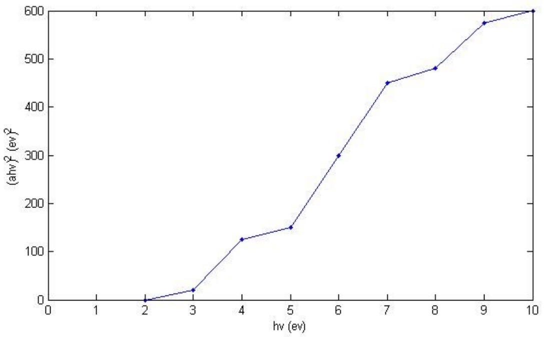

Figure 3: Band gap obtained after extrapolating the linear portion of $(\alpha h\nu)^2$ vs $(h\nu)$ curve

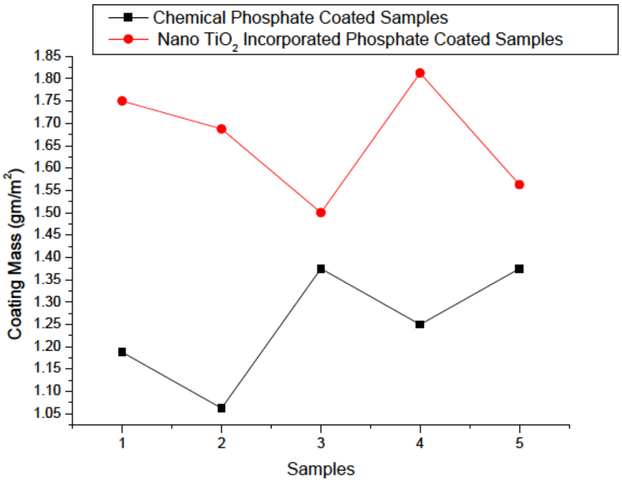

Figure 4: Comparison between coating mass.

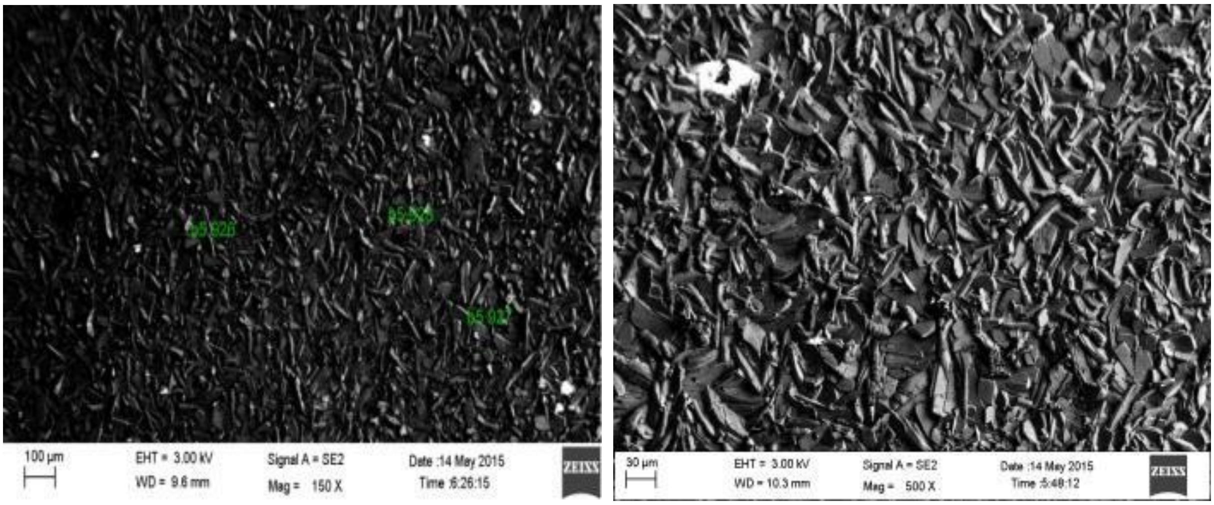

Figure 5: Scanning Electron Microscopy of chemical phosphate coatings developed using phosphating bath a) without nano-TiO_2 and b) with 2.0 g/L nano-TiO_2.

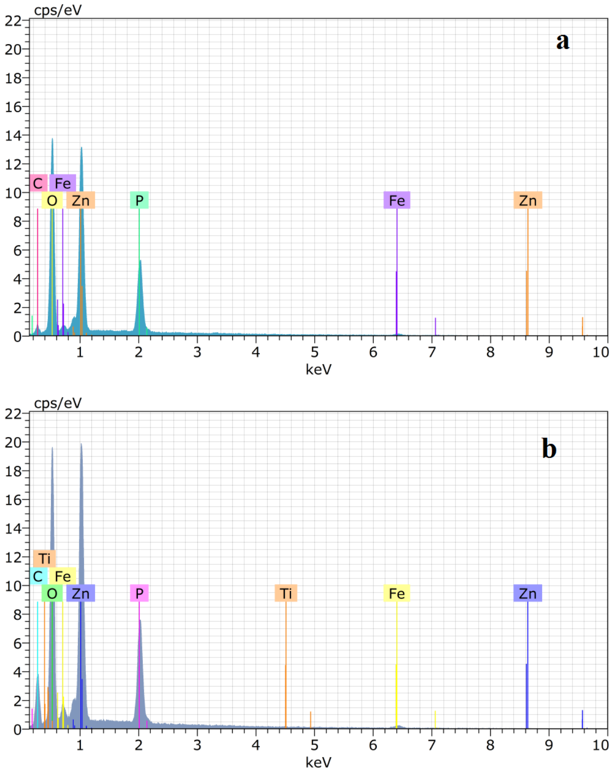

Figure 6: EDX of chemical phosphate coatings a) normal phosphating bath b) Phosphating bath with 2.0 g/L nano-TiO_2.

Characterization

The morphology of the zinc phosphate coatings deposited from baths with and without nano-TiO_2 was studied. The color of the coatings was dark grey and grey for the normal phosphate coating and the phosphate coating with nano TiO_2. Remarkable difference could be observed in the surface morphology of these two coatings. Compared to the normal phosphate coating surface the surface of TiO_2 coating was more homogeneous. The large crystals caused better surface coverage of the coatings with nano-TiO_2 (Figure 5; at the same time micropores and cavities were obtained on the surface of both the coatings. But the number of pores was less in case of the coatings with nano-TiO_2 and this may be due to the surface sealing effect brought about by nano-TiO_2 particles. The addition of nano-TiO_2 into the phosphating bath caused structural refinement of the nano-crystals in phosphate coatings morphologically and also helped to achieve maximum surface coverage.

EDX signals of the chemical zinc phosphate coatings developed using normal phosphating bath and phosphating bath with 2.0 g/L nano-TiO_2 are shown in Figure 6 and the presence of nano-TiO_2 was confirmed.

From the EDX analysis it was confirmed that nano-TiO_2 is present in the coating developed using nano-TiO_2 in the phosphating bath. EDX analysis reveals a significant increase in Zn/P ratio from 3.38 to 3.45 (Table 1) for the coatings developed by normal phosphating and nano-TiO_2 phosphate coatings which in turn lead to increase in the content of $Zn_3(PO_4)_2{\cdot}4\ H_2O$ when 2.0 g/L nano-TiO_2 is added in the phosphating bath. Further it can be concluded that increased Zn/P ratio reveals a more uniform and thick coatings which was in lieu with previous work carried out elsewhere [13].

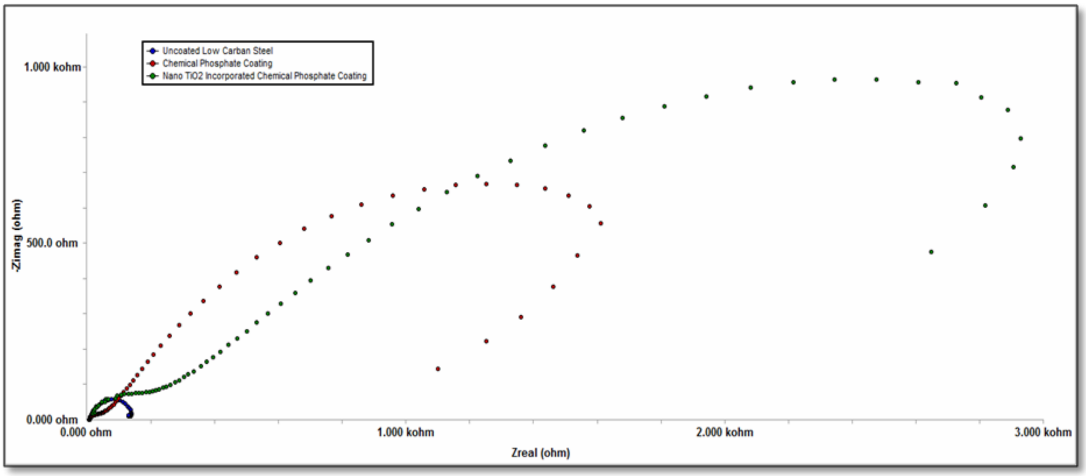

Figure 7: Nyquist plots for bare low carbon steel, normal phosphate coated and nano TiO$_2$ phosphate coated steel.

Table 1: Chemical composition of phosphate-coated samples obtained by EDX

Coating Type	**Fe**	**O**	**Zn**	**P**	**Ti**	**Zn/P**
Normal phosphate coatings	15.7	36.3	27.2	8.06	00	**3.38**
Nano-TiO$_2$ phosphate coatings	**4.59**	**38.3**	**34.3**	**9.9**	**0.13**	**3.45**

Corrosion Studies

The corrosion protection performance of the coatings was evaluated through potentiodynamic polarization technique using 3.5% NaCl solution. It is noteworthy that TiO$_2$ particles in the phosphating bath shift the corrosion potential towards positive values which reflects the improved corrosion resistance. It was found that the extent of shift in potential is largely a function of phosphate coating weight and the porosity of the coating. The samples with phosphate coatings prepared from baths containing nano-TiO$_2$ (2 g/L) showed more corrosion protection (Table 2). Phosphate coatings are generally porous in nature, which will favor adhesion of paint film on the surface. The decrease in the corrosion current for the coatings developed using nano-TiO$_2$ particles clearly indicates that the coating is more uniform.EIS studies of chemically zinc phosphate coated sample and nano-TiO$_2$ containing phosphate coated samples at 1 hours of immersion in 3.5 wt.% NaCl solution were carried out. The diameter of the high frequency semicircle in the Nyquist plot (Figure 7) for nano-TiO$_2$ phosphate coatings is bigger compared to normal chemical phosphate coating. A polarization resistance of 487.9 Ω was obtained for nano-TiO$_2$ zinc phosphate coatings; apart from that a high coating resistance (R_C) was also observed for the same coatings. On the other hand resistance of 240 Ω was obtained for normal zinc phosphate coatings, while it was as low as 138 Ω in case of the uncoated low carbon steel (Table 3). The equivalent circuit is been shown in Figure 8. Again the coating capacitance of nano-TiO$_2$ phosphate coated sample was found to be very low which in turn shows formed coating was insulating in nature. The EIS studies confirm that the corrosion behavior of phosphated substrate using nano-TiO$_2$ particles is a much more diffusion controlled process and thereby offering a higher corrosion resistance than the normal phosphate coating. TiO$_2$ particles in phosphate coatings helps to improve the surface coverage, uniformity and the thickness of the coating and decrease the porosity which improves the corrosion resistance of the phosphate coatings [5].

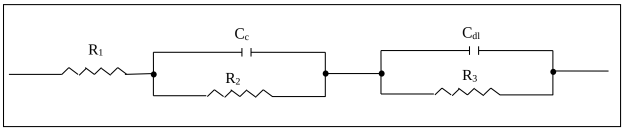

Figure 8: Equivalent circuit proposed for the impedance behaviour of nano-TiO$_2$-containing phosphate coated samples. Detailed explanation is given in text.

The impedance value is an important parameter to evaluate the corrosion protection effect of the coating for a long time interval, which directly reflects the permeating ability of the corrosion medium into the coating. The larger the impedance value, the better are the anticorrosion properties of the coating.

Table 2: Polarization parameters for bare low carbon steel, normal phosphate coated and nano-TiO_2 phosphate coated steel.

Sample	E_{corr} (mV)	I_{corr} (µA)	I_{corr} (mA/cm^2)	Corrosion Rate (mpy)
Bare low carbon steel	−731	92.70	0.0552	13.48
Normal zinc phosphate coated sample	−587	2.290	0.0308	**8**
Nano-TiO_2 phosphate coated samples	**−594**	**1.790**	**0.0274**	**3.58**

Table 3: EIS results of uncoated low carbon steel, normal phosphate coated and nano-TiO_2 phosphate coated steel.

Sample	Coating impedance (Ω)	Coating impedance (Real) (Ω)	Polarization resistance (Ω)	Coating capacitance (F)
Uncoated low carbon steel	143.7	139.5	138	**0.094**
Normal phosphate-coated sample	1796	1615	240.2	**0.058**
Nano-TiO_2 phosphate-coated sample	**3153**	**2940**	**487.9**	**0.005**

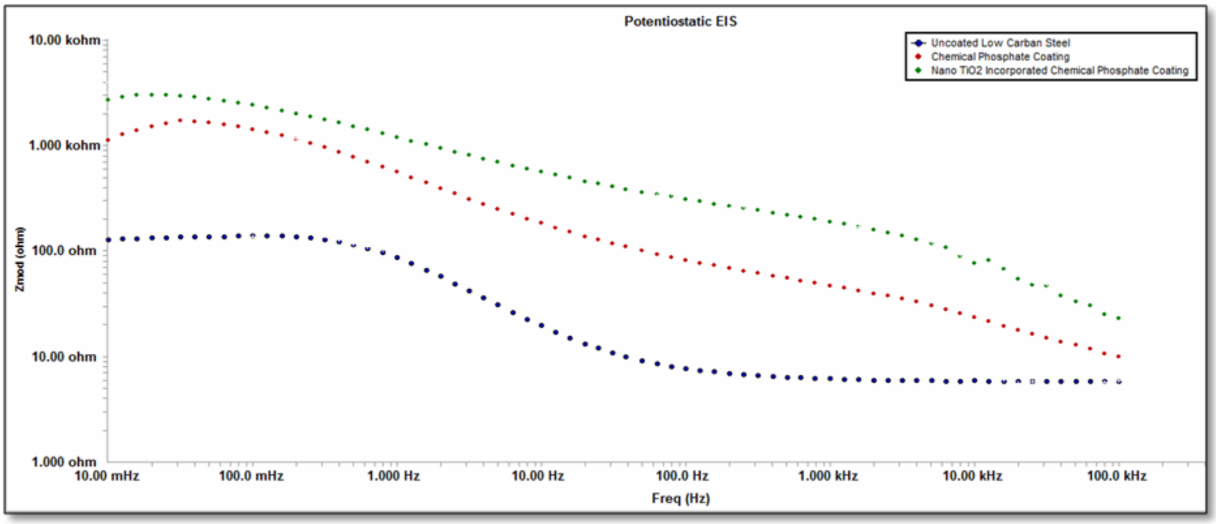

Figure 9: Bode plots for bare low carbon steel, normal phosphate coated and nano-TiO_2 phosphate coated steel.

Coating Porosity

The major problem in the use of phosphate coatings is the existence of open pores. These local defects form direct paths between the corrosive environment and the coating/substrate interface. As the corrosion reactions are initiated at the coating/substrate interface, determination of porosity is important to estimate the overall corrosion resistance of the coated materials. Electrochemical techniques can be used for porosity measurements and performance evaluation of coating substrate systems. The small potential difference between the substrate and the coating allows that the substrate current density can be used in the porosity measurement. The coating porosity can be evaluated using following equation [7]:

$$P = \frac{R_{ps}}{R_p} 10^{-\frac{\Delta E_{corr}}{\beta_a}}$$

where P is the coating porosity, R_{ps} is the polarization resistance of substrate, R_p is the polarization resistance of coated substrate, ΔE_{corr} is the potential difference between the uncoated and the coated substrate and β_a is the anodic Tafel coefficient of substrate. The electrochemical parameters were obtained by polarization studies using Gamry software (Figure 9). Corrosion potential of sample, coated substrate and anodic Tafel coefficient of substrate

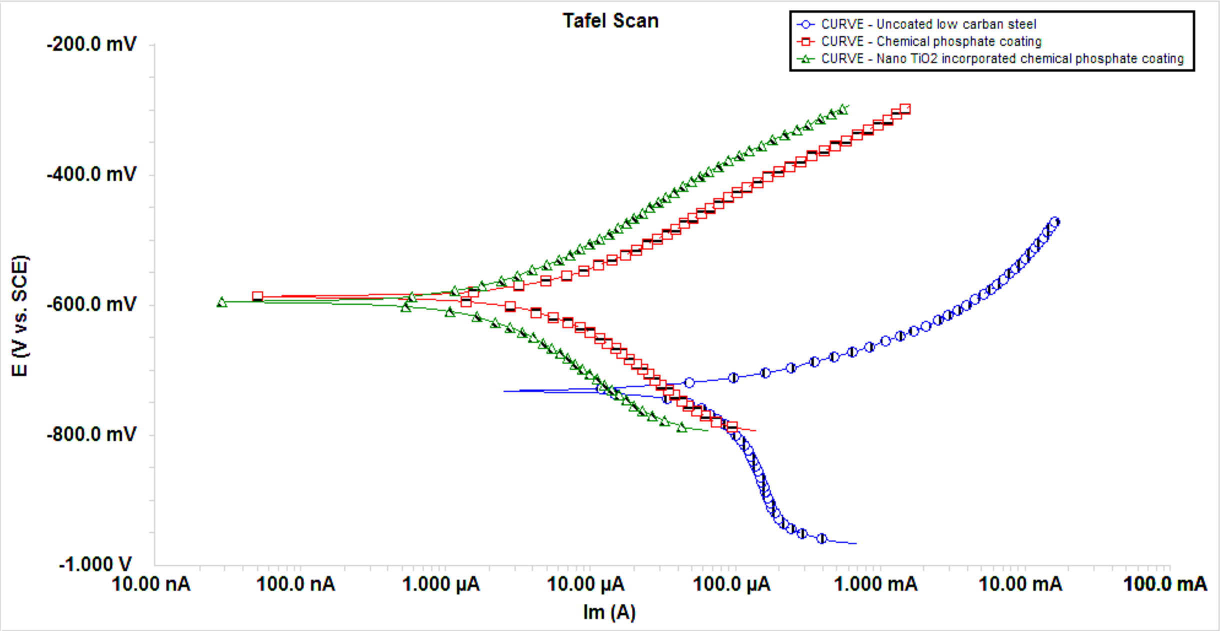

Figure 10: Potentiodynamic polarization study (Tafel plots) for bare low carbon steel, normal phosphate coated and nano-TiO$_2$ phosphate coated steel.

were obtained by potentiodynamic polarization study in 3.5% NaCl (Figure 10).

Coating porosity was found to be 0.65% and 0.32% for zinc phosphate-coated and nano-TiO$_2$ zinc phosphate-coated substrate, respectively. Significant reduction (~ 50%) in the coating porosity was observed with nano-TiO$_2$ phosphate coated substrate as compared to normal phosphate coating. This is in agreement with previous work [17] wherein porosity was fairly low, of the order of 0.5 - 1.5% of the phosphated surface.

4 Conclusions

- Chemical zinc phosphate coatings were developed on low carbon steel by using nano-TiO$_2$ in the standard phosphating bath. Significant variations were observed in coating mass, porosity and corrosion resistance.
- Incorporation of nano-TiO$_2$ in bath significantly reduced coating porosity by 50% as compared to normal phosphate coating process and had given worthy results.
- It was found in EIS studies that phosphate coatings developed by the incorporation of nano-TiO$_2$ have higher impedance (3153 Ω) and less coating capacitance (0.005 F) which in turn inhibits electrolyte penetration in the subsequent layer.
- Corrosion rate of nano-TiO$_2$ phosphate coated samples was found to be 3.5 mpy which was 4 times less than the bare uncoated low carbon steel (~14 mpy).
- To sum up, nano-TiO$_2$ particles in the phosphating solution yielded phosphate coatings of higher coating weight, higher surface coverage and enhanced corrosion resistance than the normal zinc phosphate coatings which were developed using normal phosphating bath.

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