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Study of Corrosion Behavior of Ni-P-TiO$_2$ Nanocomposite Coating on Mild Steel Deposited by Electroless Deposition Process

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Abstract

The inclusion of TiO$_2$ nanoparticles into Ni–P matrix enormously enhances their properties. In this research work, the Ni–P–TiO$_2$ nanocomposite coatings with variable TiO$_2$ concentration were prepared on mild steel using electroless coating methods and their microstructure, phase morphology, hardness and electrochemical behaviors were observed using Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), microhardness test and potentiostat respectively. FESEM images showed that TiO$_2$ nanoparticles uniformly dispersed into Ni-P matrices. XRD pattern showed that incorporation of nano TiO$_2$ particles increase amorphous nature of coating which enhance anticorrosive property of coating. Microhardness test revealed that Ni-P-TiO$_2$ nanocomposite coating enhance the hardness of mild steel. Electrochemical behavior of pure mild steel, Ni-P alloy coating and Ni-P-TiO$_2$ nanocomposite coating confirmed that introduction of TiO$_2$ nanoparticles increases the corrosion resistance of mild steel for a small amount of TiO$_2$ nanoparticles.

Introduction

The electroless coating is an autocatalytic chemical process used to deposit a layer of metal on the other substance without passing electric current in an electroless bath. The electroless bath contains an aqueous solution of metal ions, reducing agents, complexing agents, stabilizers and operating at a constant temperature and pH range. The electroless coating has numerous advantages on electrolyte coating; it enhances physical and mechanical properties of the material like it provide uniform coating thickness, increasing hardness, corrosion resistance and wear resistance [1-2]. The electroless coating can be done on any type of substrate as like steel, glass, aluminum, and alloy etc. There are many types of steels like stainless steel, mild steel, cryogenic steel, etc. Among these mild steel is used frequently because it has good tensile strength, ductility and low cost but poor corrosion resistance. It is used in all engineering purpose. This type of steel contains 0.03-0.3 wt. % carbon, and can be utilized in nearly any project that necessitates using a great amount of metal. To increase the properties of the mild steel for broadening the area of the applications; composite coating is used [3].

Nickel–phosphorous (Ni-P) is frequently used for electroless plating due to its uniform thickness of the coating, corrosion resistance, hardness and wear resistance. Nanocomposite coatings are produced by confining two types of particles one is hard and other is soft particles into electroless Ni-P matrix. If the coating composed by enclosing soft particles (PTFE, MoS$_2$, WS$_2$, HBN, and graphite) known as lubricated composite coating and if it is composed of hard particles (Al$_2$O$_3$, TiO$_2$, SiC, B$_4$C, WC, ZrO$_2$ diamond, and Si$_3$N$_4$) termed as non-lubricated composite coating [4]. The introduction of TiO$_2$ particles in the coating has added great scope in the field of research due to its massive uses in the material science. Nanoparticles of TiO$_2$ result in improving wear

and corrosion resistances [5]. This hard material is so delicate and offers less or no adhesion potential. Therefore, a metal matrix is used to hold TiO2 particles together and promote good adhesion to the metal surface to be coated. These composites have appreciably higher strength and hardness than pure metal [6].

The objective of the present work was to obtain Ni-P electroless coating with TiO$_2$ nanoparticles, to investigate their coating structure, hardness and corrosion properties. The TiO$_2$ nanocomposite coating is characterized with the help of a number of techniques such as scanning electron microscopy, X-ray diffraction techniques, Vickers microhardness testing machine and gamry potentiostat order to explain the microstructure, hardness and corrosion behavior of the Ni-P-TiO$_2$ nanocomposite coating.

Experimental

The electroless coating is mainly two step process (i) preparation of the substrate, (ii) deposition of the electroless coating. Mild steel was used for this purpose because its wide applications in daily life but has poor mechanical and electrochemical properties such as hardness,corrosion resistance etc. Deposition of Ni-P alloy coating and Ni-P-TiO$_2$ nanocomposite coating on mild steel to enhance desired properties.

In the plating procedure, samples of mild steel were cut and cleaned and pretreated followed by deposition of Ni-P and Ni-P-TiO$_2$ nanocomposite coatings were done.

Preparation of substrate

For adhered coating, it is essential to sample should be neat. For this purpose, mild steel sheet was cut into the size of 20 mm × 10 mm × 1mm rectangular shape samples and availed for Ni-P-TiO$_2$ electroless nanocomposite coating. Emery paper is used for cleaning the sample from unwanted materials.Table 1 shows the

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chemical composition of the mild steel samples obtained by optical emission spectroscopy (OES).

Table 1: Chemical compositions of mild steel

Element	C	Si	P	Ni	Al	Cu	Sn	Cr	W	Fe	As
Weight %	.085	075	.016	.119	.016	.007	.0087	3.002	.0509	96.5	.017

Deposition of electroless coating

The process of deposition of electroless coating on the mild steel is done in two steps:

1. Pre-treatment of the substrate
2. Deposition of electroless coating on the mild steel substrate.

Pretreatment of the substrate

The prepared mild steel samples were pretreated in acetone,alkaline (NaOH) and acidic (HNO₃) medium for degreasing purpose and then pretreated in SnCl₂ followed by PdCl₂ solution for few minutes for sensitizing and activation purpose sequentially with intermediate water rinses. Figure 1 shows the flow chart of pretreatment process when mild steel was pretreated in SnCl₂. SnCl₂ is reduced in Sn^{+2} and absorb at sample surface and in activation process Pd^{+2} reduced by Sn^{+2} accourding to reaction (i) and attach on the active center of the surface of the sample which can facilitate Ni metal deposition on the sample [7].
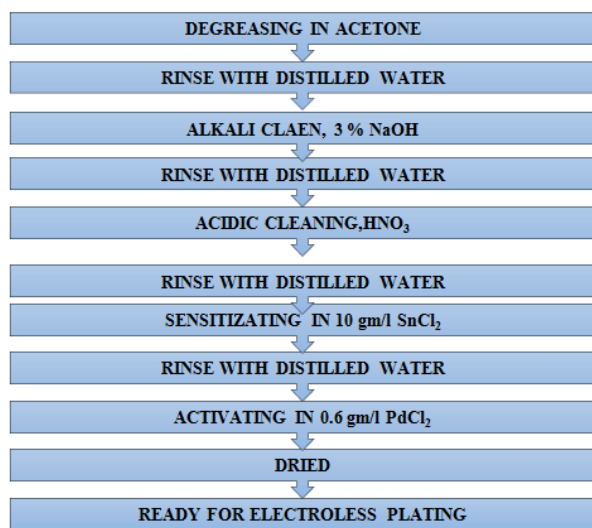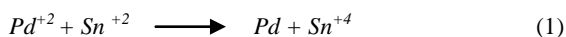
$$Pd^{+2} + Sn^{+2} \longrightarrow Pd + Sn^{+4} \qquad (1)$$

Figure 1: Pretreatment process for electroless deposition coating

Deposition of electroless coating on the mild steel

The electroless coating is done in deposition bath.The bath composition used for preparing electroless composite coating and coating conditions were given in Table 2 and Table 3 respectively.

Table 2: Compositions of the electroless coating

Compositions	Function	Concentration
NiSO₄.6H₂O	Metal source	35gm/l
NaH₂PO₂.H₂O	Reducing agent	20gm/l
CH₃CHOHCOOH	Stabilizing agent	3gm/l
TiO₂(10-25nm)	Second phase Nanoparticles	Variable

Table 4 shows functions of components and parameters used in Ni-P alloy coating and Ni-P-TiO₂ nanocomposite electroless coating.
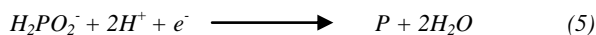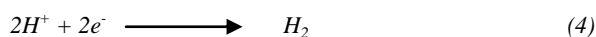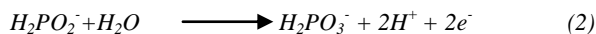
Table 3: Optimum Parameters for coating process

Deposition Parameters	
Temperature	75-80˚c
pH	2-4
Stirring speed	50 rev/min
Deposition time	1 hour
Bath volume	200 ml
Bath loading	0.2 m²/l

Table 4: Components and parameters of bath and their functions [8].

Component/ Parameter	Function
Metal- ions	Source of metal
Reducing-agents	Provide electrons to reduce the metal ions
Stabilizers	Stabilize the bath from decomposition by shielding catalytically active deposition
pH regulators	pH adjustment
Temperature	Energy for deposition

Figure 2 shows the basic diagram of electroless coating which is used in present research work. Following reactions are involved in electroless bath [9].

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \qquad (2)$$

$$Ni^{+2} + 2e^- \longrightarrow Ni \qquad (3)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (4)$$

$$H_2PO_2^- + 2H^+ + e^- \longrightarrow P + 2H_2O \qquad (5)$$

The deposition process was executed for 1 hr., at a constant temperature (80°c) and pH (2-4) [1]. After completion of deposition process sample was rinse with distilled water and dried.
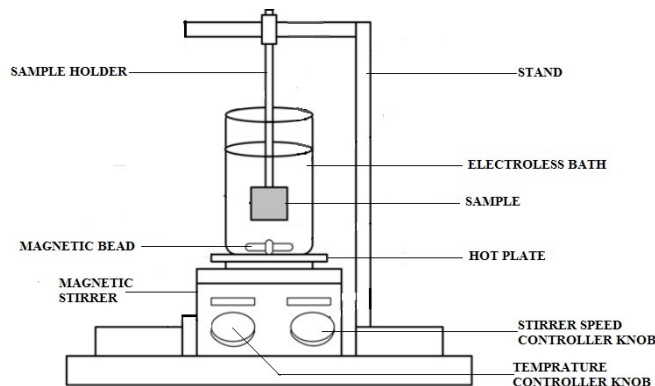

Figure 2: Basic diagram of apparatus used in electroless coating experiment

Results and Discussion

After the Ni-P and Ni-P-TiO₂ nanocomposite coating, several characterizations were done for find out different parameters such as surface morphology, phase morphology, hardness and corrosion resistance by the help of field emission scanning electron microscopy (FESEM), X-ray diffraction microscopy (XRD), Microhardness tester and potentiostat respectively. The detail explanations of these tests are following:

Surface Morphology

In order to investigate the morphology of Ni-P and Ni-P-TiO₂ nanocomposite coating, field emission scanning electron microscopy was used.

In Figure 3, Ni-P alloy coating and Ni-P-TiO₂ coating with different compositions of TiO₂ nano particles is represent.
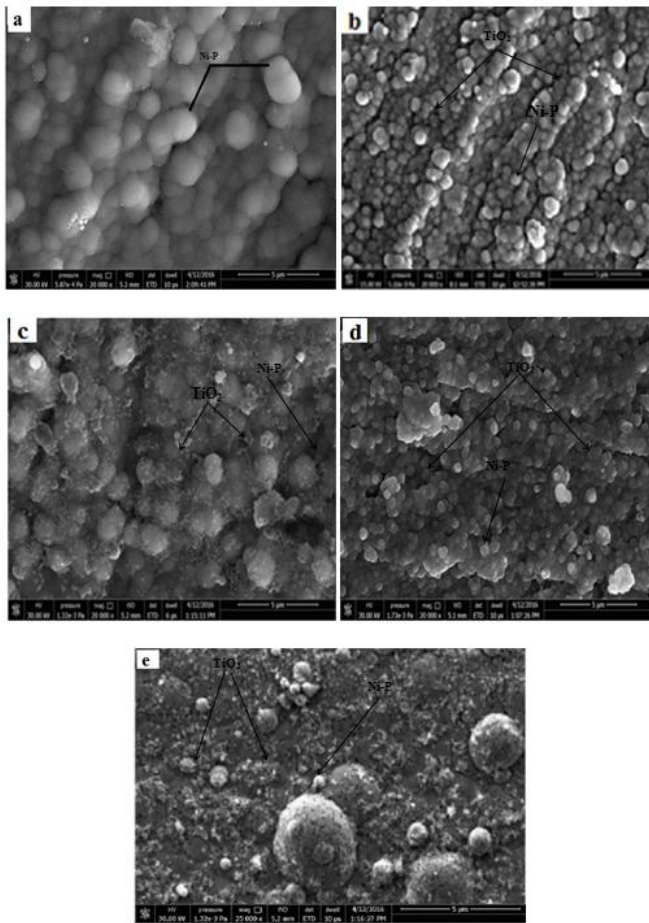

Figure 3: Field emission scanning electron microscopy images of Ni-P and Ni-P-TiO₂ composite coatings with various nano TiO₂ particles concentration with (a) absence of TiO₂ ; (b) 6gm/l TiO₂ ; (c) 8gm/l TiO₂ ;(d) 10gm/l TiO₂ and (e) 12 gm/l TiO₂.

The plating showed that the typical spherical nodular structure of Ni-P and dispersed second phase of nano TiO₂ particles. Figure 3(a) showed the Ni-P coating and figure 3(b, c, d, e) showed that the titanium oxide nanoparticles were successfully dispersed in Ni-P alloy matrix. The concentration of TiO₂ nanoparticles increases with the concentration of TiO₂ in bath 10gm/l (figure 3(d)). It has been found that beyond 10gm/l saturation occurred; there is no change after 10gm/l bath concentration because after this concentration of TiO₂ nanoparticles, reaction is done with the surface of the container. Various factors affect the adding of TiO₂ particles in a Ni–P matrix incorporating, particle geometry and relative density, concentration of particles in the deposition bath and orientation of the part being coated [10,11].

Phase Morphology

X-ray diffraction technique is used to characterize Ni-P and Ni-P- TiO₂ nanocomposite coating. The range of the diffraction angle 2Θ is 10˚to 90˚. In figure 4, comparative study of X- ray diffraction pattern of Ni-P alloy coating and Ni-P-TiO₂ nanocomposite coating are present.

In Ni-P coating peak of Ni appears at 45.1184˚ (2, 1, 7) and the peak of TiO₂ appear at 27.1500˚ (1, 1, 1) lattice structure of NI-P is Rhombohedral. NI-P coating shows amorphous nature of coating due to high phosphorous content in it. X-ray diffraction results

show that with a broad peak of microcrystalline Ni, small peaks of TiO₂ are also present. Lattice parameters for Ni-P and Ni-P-TiO₂ nanocomposite coating are $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$ and $\alpha = 90°$, $\beta = 119.62°$, $\gamma = 90°$ respectively according to standard JCPDF card. Figure 5 shows that as the amount of TiO₂ increases peak of Ni shifted towards right slightly and small peak represents TiO₂ content in the coating which is not sharp due to oxide content and peak height increases with TiO₂ content in deposition bath.
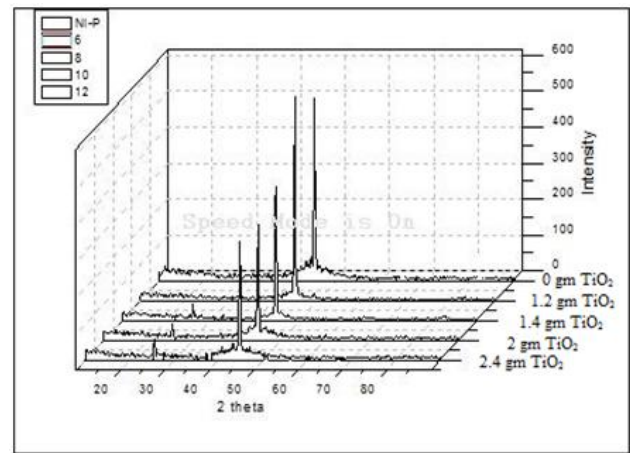

Figure 4: Comparative study of X-ray diffraction pattern of Ni-P and Ni-P-TiO₂ nanocomposite coating

Amorphous nature of coating is increases due to addition of nano TiO₂ particles in Ni-P matrix which improves corrosion resistance of the sample.

Microhardness

For the measurement of hardness of coated samples, Vickers microhardness testing machine was used. The hardness of the mild steel is very low; it can be increased by deposition of the coating. Microhardness of mild steel, Ni-P coating, and the Ni-P-TiO₂ nanocomposite coating was measured and comparison between them was done. Microhardness tester showed that as an increase in the concentration of TiO₂ nanoparticles, a hardness value of the coating sample is an increased. Fig 5 shows a graphical representation of hardness value of mild steel with variable concentration of TiO₂ nanoparticles.
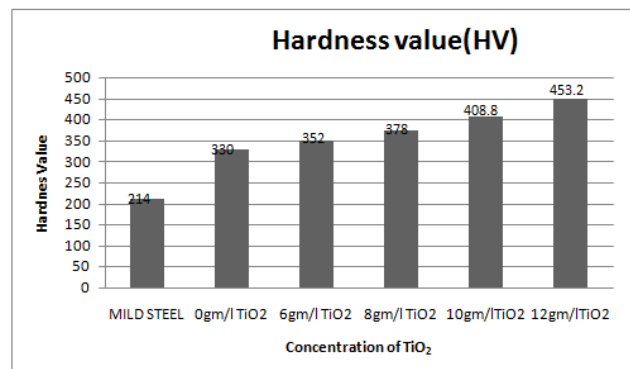

Figure 5: Graphical representation of hardness value, on X - axis and Y-axis content of TiO₂ in deposition and hardness value in VHN (vickers hardness number) are present respectively.

Results of microhardness tester showed that incorporation of TiO₂ nanoparticles increases the hardness of mild steel. Microhardness value of Ni-P-TiO₂ reached 453.2 VHN and microhardness values of Ni-P coating and mild steel is 330 VHN

and 214 VHN respectively on 15 gm. load applied for 10 seconds. Nanoparticles of TiO$_2$ deposits in Ni-P matrix facilitated to prevent the plastic deformation of Ni-P matrix and hence enhance microhardness of mild steel [12].

Corrosion resistance

Measurement of corrosion resistance was done by the help of gamry reference 600 potentiostat to obtain electrochemical behavior of composite coating. Coated samples were kept in 3.5 wt. % of NaCl solution to find out corrosion resistance. After this the corrosion potential and current density for electroless Ni-P alloy coating and Ni–P–TiO$_2$ nanocomposite coating were measured current density reduce with the addition of nano TiO$_2$ particles.

Formulation for finding polarization resistance is given [13, 14] in equations (6),

$$Polarization\ resistance\ (R_p) = \frac{\beta}{Icorr} \qquad (6)$$

β is the reaction tafel constant (volts/decade) which can be measured by equation (7)

$$\beta = \frac{\beta a \beta c}{2.3(\beta a + \beta c)} \qquad (7)$$

In a corrosion system, there is two opposing reactions anodic and cathodic. βa and β$_c$ are anodic and cathodic tafel constants respectively.

Corrosion rate of the sample can be finding out by equation (8)

$$Corrosion\ rate\ (C.R.) = \frac{0.13Icorr(EW)}{d} \qquad (8)$$

Corrosion rate in milli-inch per year (mpy).
I_{corr} is corrosion current density (μA/cm^2).
EW is the equivalent weight (gm/equivalents).
d is the density in gm/cm^3.

Figure 6 shows comparative study of electrochemical behavior of mild steel, Ni-P alloy coating and Ni-P-TiO$_2$ nanocomposite coating with variable nano TiO$_2$ particles concentration.
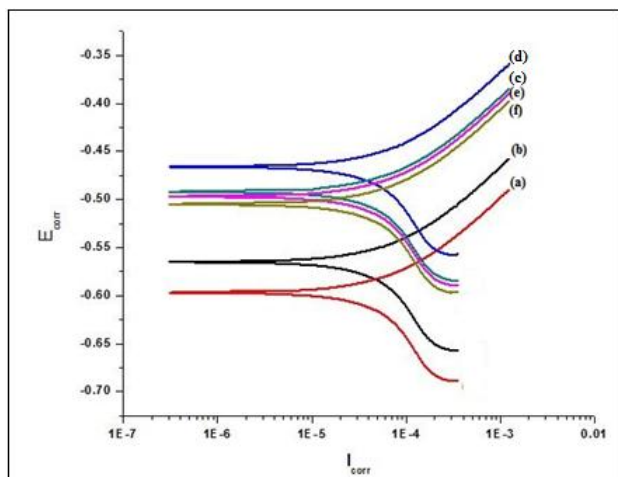

Figure 6: comparative study of electrochemical behavior of (a) mild steel, (b) Ni-P alloy coating and Ni-P-TiO$_2$ nanocomposite coatings with (c) 6gm/l TiO$_2$, (d) 8gm/l TiO$_2$, (e)10gm/l TiO$_2$, (f) 12 gm. /l TiO$_2$

Comparative study of electrochemical behavior of mild steel, Ni-P alloy coating and Ni-P-TiO$_2$ nano composite coating with variable TiO$_2$ nanoparticles concentration shows that the electrode

potential(E_{corr}) of Ni-P-TiO$_2$ firstly increases up to 8gm/l and after this concentration decreases continuously. The value of electrode potential (E_{corr}) of mild steel (a) is -650mv, E_{corr} of Ni-P alloy coating (b) is -556mv, E_{corr} of 6gm/l TiO$_2$ coated sample (c) is -463mv and E_{corr} of Ni-P-TiO$_2$ nanocomposite coating with 8 gm/l TiO$_2$ (d) is -454mv and then decreases, E_{corr} of electroless nanocomposite coating with 10gm/l TiO$_2$ coated sample (e) is -470 mv and 12 gm/l TiO$_2$ coated sample (f) is -515 mv. Corrosion current density (I_{corr}) is also reducing up to 8gm/l and then increases. I_{corr} of mild steel (a) is 97μA/cm^2,I_{corr} of Ni-P (b) is 85μA/cm^2, I_{corr} of 6gm/l TiO$_2$ coated sample (c) is 51μA/cm^2 and I_{corr} of electroless nanocomposite coating with 8gm/l TiO$_2$ (d) is 48μA/cm^2 and I_{corr} of Ni-P-TiO$_2$ (e) nanocomposite coating with 10gm/l TiO$_2$ 53μA/cm^2 and Ni-P-TiO$_2$ with 12 gm./l TiO$_2$ (f) is high and it is 56μA/cm^2. Polarization resistance increases up to 8 gm/l TiO$_2$ and then decreases after this and corrosion rate also decreases up to 8 gm./l and then increases after this. Figure 7 shows that polarization resistance increases and corrosion rate decrease but at higher concentration of TiO$_2$ corrosion resistance decreases and corrosion rate increases. Titanium particles in the coating work as a physical barrier and shield the small openings, gaps and micro holes on the coated surface. This enhances the anti-corrosion property of nanocomposite coating but for a small amount of TiO$_2$ nanoparticles. The reason behind this may be that when TiO$_2$ concentration increases in the bath it increases the hardness and porosity and coating becomes loose. The corrosive media easily penetrate coating from these pores and decrease the corrosion resistance.
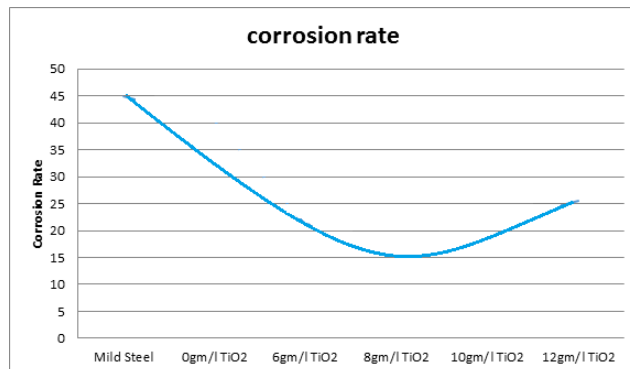

Figure 7: Graph of corrosion rates v/s different concentrations of TiO$_2$ nanoparticles

The above experiments results indicate that mechanical properties of mild steel significantly enhanced by electroless Ni-P alloy coating and Ni-P-TiO$_2$ nanocomposite coating on it. XRD pattern results show that incorporation of TiO$_2$ nanoparticles in Ni-P matrix reduces the crystalline nature of the coating and coating becomes amorphous in nature which can improve the corrosion resistance of mild steel substrate so these coatings can be used in corrosive environments. Nanoparticles of titanium oxide dispersed in Ni-P matrix which was proved in field effect scanning electron microscopy images, prevent the plastic deformation of mild steel and hence enhance microhardness of the mild steel. Increasing the TiO$_2$ nanoparticles microhardness of the coating is increased with coating becomes loose and porous due to this corrosion resistance decreases because corrosive media enter in to the coating, due to this corrosion rate decreases for small amount of TiO$_2$ nanoparticles and then increases.

Conclusions

The Ni-P-TiO$_2$ nano compositing coating was successfully prepared by including nano TiO$_2$ particles with size ranges from 10-25 nm in the Ni-P matrix using electroless coating method. The experimental data shows that as TiO$_2$ composition increases in

deposition bath properties of mild steel enhanced. In X-ray diffraction pattern Ni peak shifted towards the right and another peak of TiO_2 also found which increase with the TiO_2 composition in deposition bath. Microhardness of the substrate has been significantly improved. Hardness value of mild steel is 214 VHN (Vickers hardness number) and hardness value of Ni-P alloy coating is 330 VHN. Incorporation of TiO_2 nanoparticles enhances the hardness value up to 453.2VHN. Corrosion rate decreases and corrosion resistance increases but at certain point polarization resistance starts decreasing and corrosion rate starts increasing. Due to these properties Ni-P-TiO_2 nanocomposite coating is better than Ni-P coating and finds a wide range of applications in all fields.

Acknowledgements

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