Journal of Materials Science & Surface Engineering Vol. 4 (5), 2016, pp 432-435

Contents lists available at http://www.jmsse.org/

Journal of Materials Science & Surface Engineering

Characterization Study of Ni-P-TiO_2 Nanocomposite Coating on Mild Steel by Electroless Plating Method

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Article history

Received: 16-Aug-2016
Revised: 26-Aug-2016
Available online: 19-Sep-2016

Keywords:
Electroless;
Composite coating;
Corrosion resistance;
Surface-morphology;
Chemical bath deposition.

Abstract

Surface engineering is the need of the modern society due to it deals with different properties of materials which are used in daily life applications. Autocatalytic coating i.e. electroless coating is one of the ways of modify surface of materials and improves their properties i.e. metallurgical, mechanical etc. In this research work, comparative studies of electroless Ni-P, Ni-P-TiO_2 Micro-composite and Ni-P-TiO_2 nanocomposite coating are studied. The deposited coating were characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray diffraction, Vickers micro-hardness. Corrosion resistance was studied by potentiodynamic polarization in 3.5% sodium chloride solution. Results showed that embedded nanoparticle of TiO_2 in coating caused increase of corrosion resistance and microhardness. The improvement in surface properties of composite coatings will have numerous industrial applications in aerospace, marine, automotive, oil and gas production, military etc.

Introduction

The material for making components may be chosen based on its forging, forming, machinability and strength [1]. A subsequent surface coating on the component material extends their service life. Surface coatings provide protection from corrosion, erosion, and abrasion. By applying different kinds of coatings, different performance characteristics could be achieved simultaneously [2, 3].

Surface coating is activity used to enhance the properties of the surfaces of engineering components increasing the functionality and service life of the components [4]. The ability to co-deposit fine particulate matter with electroless Ni–P matrix to prepare composite coatings is a key development in this area of research as they extend the potential of electroless nickel coatings for innumerable applications [5]. Numerous studies are available on the development of electroless Ni–P composite coatings with the incorporation of various hard and soft particles, emphasizing the mechanism of particle incorporation, factors influencing particle incorporation and the effect of particle incorporation on hardness, friction, wear resistance, abrasion resistance, corrosion resistance, etc [5, 6]. Ni-P coating is one of the most effective and widely used electroless coatings for mild steel [6]. When nano TiO_2 and micro TiO_2 particles are used to form composite coatings the result is an improved microstructural and mechanical properties of the substrate [8]. Ni-P-TiO_2 composite coatings on Al-alloy produce good surface morphology and good resistance to corrosion in marine atmospheres. No study could be found in the literature on the Ni-P composite coating containing TiO_2 particles on mild steel substrate.

Present study is therefore made to understand the influence of the electroless coatings on the surface marphology and mechanical behaviour of the mild steel substrate. Ni-P-NanoTiO_2 and electroless Ni-P-MicroTiO_2 composite with different concentration of TiO_2 particles were coating on mild steel substrates has been investigated.

Experimental

In present work steel substrates having general composition Fe-3Cr-0.08C were used to study the effect on electroless Ni-P coating, Ni-P-NanoTiO_2 composite coating and Ni-P-MicroTiO_2 composite coating of the microstructural, mechanical and corrosion resistant properties. The substrate size was taken as 20mm x 10mm x 1mm. The chemical analysis of the substrate which is shown in Table 1 by using Optical Emission Spectrometer (Bench type).

The following pretreatment process has been carried out for the obtain adhered electroless deposition:

- Degreasing in acetone
- Rinsed with distilled water and dipped in 3% NaOH solution.
- Rinsed with distilled water followed treated with 10gm $SnCl_2$ solution.
- Rinsed with distilled water followed by dipped in 0.6 gm/l $PdCl_2$ solution.

Table 1: Chemical Composition of mild steel sample (wt %)

Al	C	Si	P	Fe	Cr	Ni
0.0476	0.0821	0.129	0.0289	95.3	3.46	0.672

Table 2: Electroless bath chemical composition for Ni-P-TiO_2 composite coating.

Chemicals	Concentration
Nickel sulphate	35 g/L
Sodium Hypophosphite	20 g/L
Lactic Acid	5 ml/L
TiO_2 particles	10, 8, 6, 4 g/L

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Now, substrate was ready for the electroless coating. The bath composition used for preparing Ni–P-TiO_2 composite coatings is given in Table 2. The pH value of the solution was kept 4 and the temperature was maintained at 90 ± 2 °C.

Ni–P-NanoTiO_2 and Ni–P-MicroTiO_2 composite coatings on mild steel substrates with varying nano TiO_2 and micro TiO_2 content respectively were done by Chemical Bath Deposition (electroless coating) method. In this process continuous stirring using magnetic stirrer was done to disperse the TiO_2 particles in the solution. The size used for nano TiO_2 and micro TiO_2 particles are 10-20 nm and 1-10 µm respectively.

After obtaining coating, the coated sample subjected to characterization as:

The XRD was carried out on Panalytical X Pert Pro using Cu as the anode material with K alpha wavelength of 1.54Å. The size of the samples was 20mm x 10mm x 1mm. The scan range was 20˚-60˚ and the scan rate was 2˚ per minute. Microstructural characterization study was done with field emission scanning electron microscope with Energy Dispersive X-Ray Spectroscopy (EDS) (Model- Nova Nano FESEM 450). The images were taken in secondary electron (SE) mode. Surface roughness of coated steel was studied by Multimode Scanning Probe Microscope. Corrosion resistance studies of the coated steels were carried out with Gamry 600^{TM} Potentiostat/Galvanostat. Tafel electrochemical measurements were taken on the coated steel during their exposure to an aqueous solution of 3.5% NaCl at room temperature in the range of -0.4 to 0.4V open circuit potential and a constant scan rate of 1 mV/s. For comparison the corrosion studies have been applied for mild steel substrate, Ni-P coating, Ni-P-NanoTiO_2composite coating and Ni-P-MicroTiO_2composite coating.

Results and Discussion

The X-ray diffraction patterns of Ni-P and Ni-P-TiO_2 composite coatings deposited by electroless method exhibited a single broad peak corresponding to Ni (1 1 1) phase and diffused peaks revealing amorphous nature of coatings (Figure 1). This revealed that the incorporated second phase particles had negligible influence on the structure of electroless Ni-P matrix. It can be seen that both Ni-P and Ni-P-TiO_2 composite coatings were amorphous in nature. The various X-ray diffraction patterns compared in Figure 1(a) also shows the shifting of position (2θ) towards right i.e. at higher angle in case of Ni-P-NanoTiO_2 composite coatings. The reason for shifting of the peak may be due to the atomic radius of nanoTiO_2 particles being very small as compared to atomic radius of Ni-P particle. When these particles were incorporated in Ni-P matrix they decrease the inter-planar spacing as a result the lattice parameter decreased which shifts the peak towards right while in case of Ni-P-MicroTiO_2 composite coatings results show the shifting of position (2θ) towards left i.e. at lower angle. The reason for shifting of the peak may be due to the atomic radius of microTiO_2 particles being large as compared to atomic radius of Ni-P particle. When these particles were incorporated in Ni-P matrix they increase the inter-planar spacing as a result the lattice parameter increased which shifts the peak towards left [7].

The results from EDS analysis and FESEM for Ni-P, Ni-P-NanoTiO_2 and Ni-P-MicroTiO_2 composite coatings are presented in figure2(a), 2(b) and 2(c) respectably.At first, globules were formed at some random place on the mild substrate after then these globules grew in the lateral direction on the substrate. As the first layer of globules growth completed, second layer of globules deposited on previous layer. By this continuous process a coherent uniform Ni-P coating developed on steel substrate. The results show that Ni-P-MicroTiO_2 composite coatings at higher concentration of Micro TiO_2 particles (2gm) had the highest coating thickness, adding Micro TiO_2 particles to the chemical bath increased the thickness of Ni-P-MicroTiO_2 composite coatings which revealed adding Micro TiO_2 particles enhance the coating deposition rate, same as in case of Ni-P-NanoTiO_2 composite coatings.

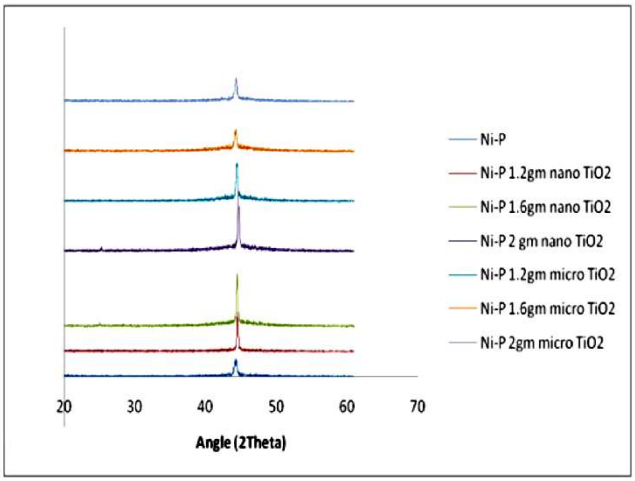
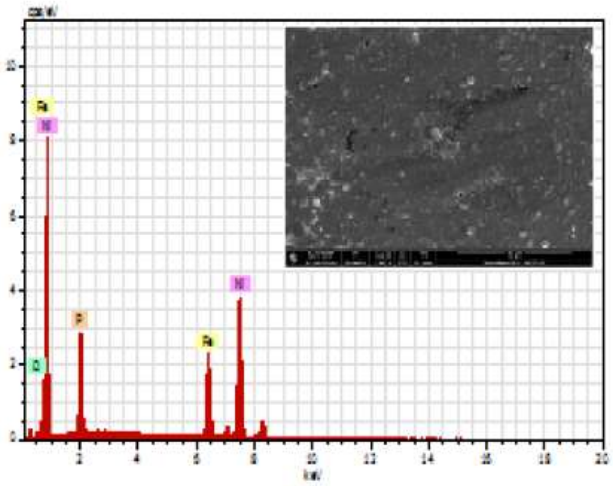
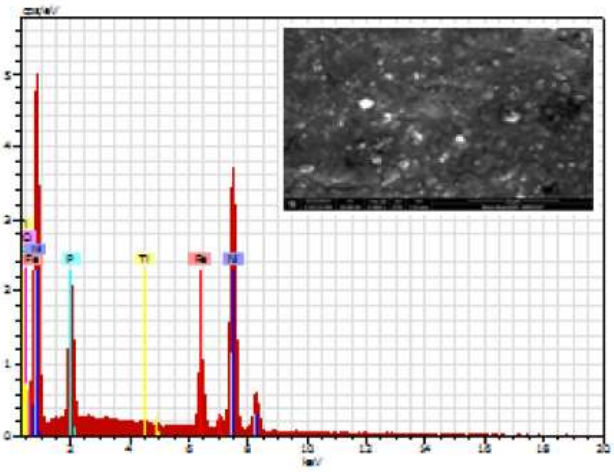


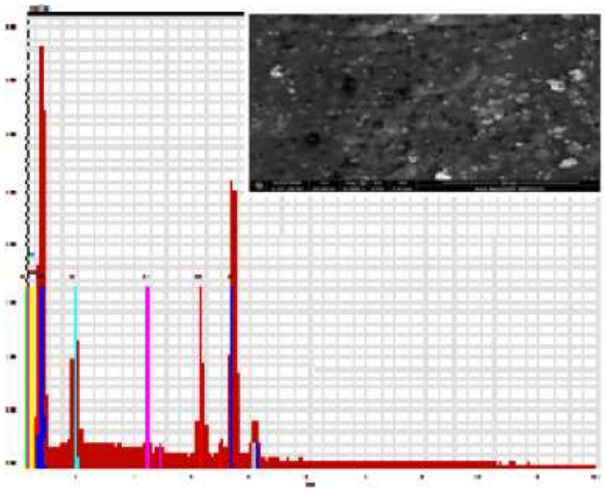
Figure 1: XRD pattern comparison of all coated samples



(a)



(b)



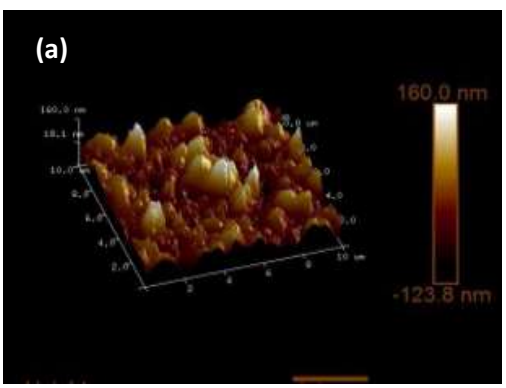
(c)

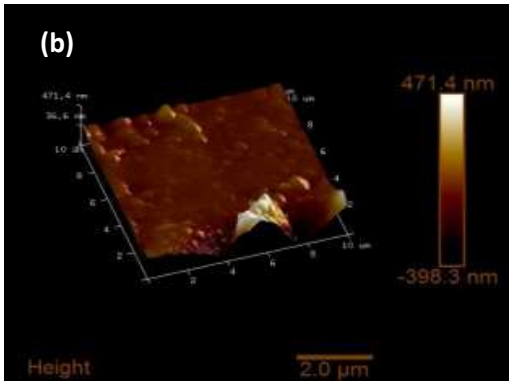
Figure 2: (a) EDS Pattern of Ni-P coating with FESEM image of electroless Ni-P coating on Mild steel substrate (b) EDS Pattern of electroless Ni-P-NanoTiO_2 composite coating on Mild steel substrate with FESEM image (b) EDS Pattern of electroless Ni-P-MicroTiO_2 composite coating on Mild steel substrate with FESEM image

Surface texture is an important issue when the main interest is to understand the nature of material surfaces as it plays an important role in the functional performance of many engineering components. The surface roughness parameters were calculated from the analysis of AFM images as shown in figures 3.

From Figure 4, it is clear that Ni-P-NanoTiO_2 composite coating had minimum surface roughness as compared to Ni-P and Ni-P-MicroTiO_2 composite coatings. The reason may be due to the use of nano TiO_2 particles which get well dispersed into the Ni-P coating matrix and imparts better surface finish. Whereas the surface roughness of Ni-P-MicroTiO_2composite coatings was found to be maximum this might be due to fewer tendencies of micro TiO2 particles to incorporate with Ni-P coating matrix. Also an increase in the roughness value was observed with the increase in the concentration of TiO_2 particles from 1.2gm to 2gm in Ni-P-NanoTiO_2 coatings as well as Ni-P-MicroTiO_2 coatings. The agglomeration of TiO_2 particles at higher concentration might be the possible reason for this increase in roughness [9, 10].

The corrosion studies were carried out in 3.5% NaCl solution with the electroless Ni-P, Ni-P-NanoTiO_2 composite coatings and Ni-P-MicroTiO_2 composite coatings. Tafel plot obtained from electrochemical potentiodynamic polarization was used to measure corrosion rate with the help of Tafel slop at anodic polarization β_a, Tafel slop at cathodic polarization β_c, corrosion current density I_{corr} and corrosion potential E_{corr}.





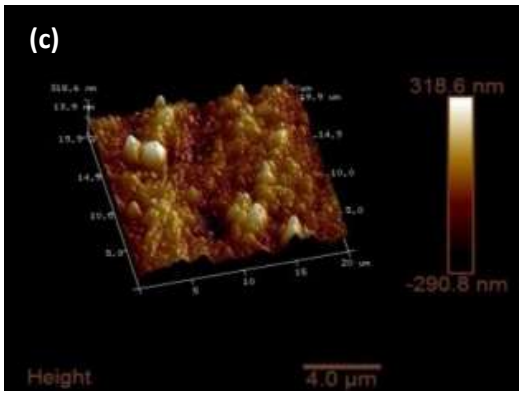


Figure 3: 3D AFM images of surface roughness of (a) Ni-P coating, (b) Ni-P-NanoTiO_2 composite coatings & (c) Ni-P-MicroTiO_2 composite coatings.

The Tafel plot is based on mixed potential theory. Table 3 has shown the electrochemical parameters of the coatings derived from the Tafel plots.

Table 3: Electrochemical parameters of mild steel substrate, Ni-P and Ni-P-TiO_2 composite coating derived from the Tafel plots.

Sample	βa (V/decade)	βc (V/decade)	Icorr (µA/cm^2)	Ecorr (mV)	Polarisation resistance (kΩcm^2)	Corrosion Rate (mpy)
Substrate - Mild steel	0.210	0.115	63.70	-583	0.507	15.14
Ni-P	0.104	0.240	25.90	-403	1.126	6.16
Ni-P-NanoTiO_2 (1.2gm TiO_2 particles)	0.093	0.442	23.70	-386	1.415	5.65
Ni-P-NanoTiO_2 (1.6gm TiO_2 particles)	0.109	0.186	18.80	-387	1.583	4.47
Ni-P-NanoTiO_2 (2gm TiO_2 particles)	0.140	0.274	10.90	-399	3.69	2.58
Ni-P-MicroTiO_2 (1.2gm TiO_2 particles)	0.505	0.240	30.60	-417	1.031	7.27
Ni-P-MicroTiO_2 (1.6gm TiO_2 particles)	0.053	0.066	10.00	-378	4.19	2.36
Ni-P-MicroTiO_2 (2gm TiO_2 particles)	0.112	0.253	19.60	-438	1.722	4.674

It was clear from the potentiodynamic results that the mild steel substrate had lowest polarization resistance and maximum corrosion rate. The corrosion density of the mild steel substrate (Icorr = 63.70µA/cm^2) was lowered by coating the mild steel

substrate with Ni-P alloy (Icorr 25.90µA/cm^2) with a protection efficiency of 60% indicating that, the Ni-P deposits have positive effects on reducing the corrosion rate in the active corrosion region. Generally, nickel electroless plating improve the corrosion resistance due to the formation of protective layer of metallic nickel and nickel phosphide that acts as a barrier for oxygen diffusion on the metal surface [11,12].

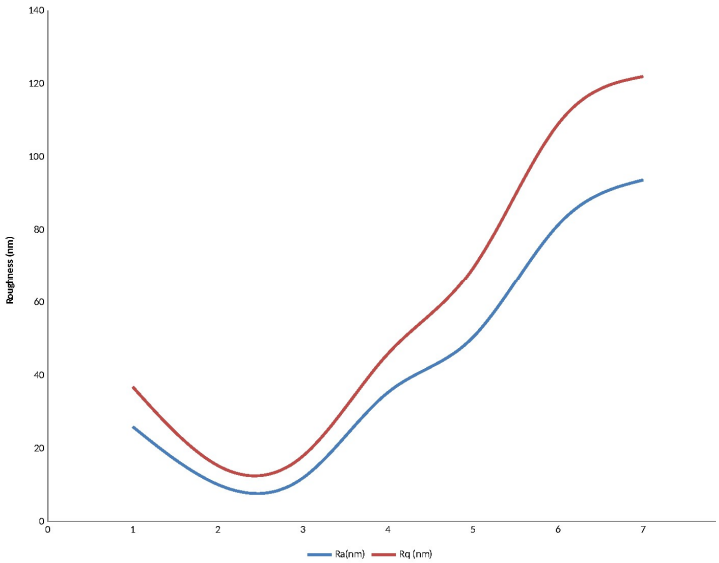


Figure 4: Graph showing the variation of Average Roughness (R_a) and Root Mean Square Roughness (R_q) for Ni-P coating, electroless Ni-P-NanoTiO$_2$ composite coating and Ni-P-MicroTiO$_2$ composite coating with varying concentration of TiO$_2$ particles. On the x-axis point 1, point 2, point 3, point4, point5, point 6 and point 7, showing Ni-P coating, Ni-P-1.2 gm nano TiO$_2$, Ni-P-1.6 gm nano TiO$_2$, Ni-P-2 gm nano TiO$_2$, Ni-P-1.2 gm micro TiO$_2$, Ni-P-1.6 gm micro TiO$_2$ and Ni-P 2 gm micro TiO$_2$ coating respectively.

The incorporation of nano TiO_2 particles in the coating caused further decrease in the corrosion current density (Icorr=23.70µA/cm^2, Icorr=18.80µA/cm^2 and Icorr=10.90µA/cm^2) and the incorporation of micro TiO_2 particles in the coating cause further decrease in the corrosion current density (Icorr= 10.00µA/cm^2) .The result of Ni-P-MicroTiO$_2$ composite coatings show higher value of Icorr for 1.2gm and 2gm TiO_2 concentration (Icorr= 30.60 µA/cm^2 & Icorr= 19.60µA/cm^2 respectively) than Ni-P-NanoTiO$_2$ composite coatings for same TiO_2 particle concentration. The corrosion testing confirmed that all coated samples of electroless Ni-P and Ni-P-TiO_2 composite coatings showed better corrosion resistance than the substrate (mild steel). Electroless Ni-P coating & electroless Ni-P-TiO_2 composite coating acts as a barrier and protects the substrate by sealing it off from the corrosive environment rather than by sacrificial action, so the coatings can be widely used in a variety of environments [13, 14].

Conclusions

FESEM and EDS analysis carried out on Ni-P-TiO_2 composite coatings revealed that Ni-P globules were covered by TiO_2 film, so it can be inferred that mild steel substrate can be protected by Ni-P-TiO_2 composite coatings better than Ni-P coatings. XRD results obtained for Ni-P coating as well as Ni-P-TiO_2 composite coatings both exhibited a single broad peak corresponding to Ni (1 1 1) phase, indicated the amorphous nature of coatings. XRD results also revealed that co-deposited second phase particles (TiO_2) did not influence the structure and phase transformation behaviour. Electroless deposited composite coatings exhibited an amorphous structure of Ni-P matrix in which crystalline titanium oxide was incorporated. AFM results revealed that Ni-P-NanoTiO$_2$ composite coating had smoother and fine surface compared to Ni-P and Ni-P-MicroTiO$_2$ composite coatings, also as the coating thickness increased the roughness of surface got increased. The results obtained from Tafel graphs confirmed that all coated sample showed improved corrosion resistance than the mild steel substrate in 3.5 wt% NaCl solution.

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