

Corrosion Behavior of Coarse- and Fine-Grain Ni Coatings Incorporating NaH₂PO₄.H₂O Inhibitor Treated Substrates

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Plain carbon steel substrates were treated with NaH₂PO₄.H₂O inhibitor for 24 hours and coated with Ni using dc and pulse electrodeposition in standard Watt's bath. The effect of dc and pulse electrodeposition, on the microstructure and corrosion properties of Ni coatings in 3.5 wt% NaCl solution was studied. The effect of inhibitor on the deposition process and corrosion behavior was also examined. Materials characterization was performed using field emission scanning electron microscopy, cross-sectional scanning transmission electron microscopy, atomic force microscopy, x-ray diffraction and nanoindentation. Experimental results indicated that pulse electrodeposition produced fine grained Ni coatings that showed lower corrosion rate compared to coarse grained dc electrodeposited Ni. Pre-treatment of substrates with inhibitor did not adversely affect the deposition process and adherent Ni coatings were readily developed. The results showed that pulse electrodeposition could be used to produce hard corrosion resistant Ni coatings while the inhibitor treatment yielded enhanced corrosion protection by providing a protective buffer layer between the Ni coating and the substrate.

Keywords: corrosion, microstructure, Nickel (Ni), electrodeposition, inhibitor, NaH₂PO₄.H₂O, sodium dihydrogen orthophosphate

1. Introduction

Nickel is commonly employed to enhance surface properties of various materials using electroless or electrolytic methods¹⁻³. Nickel is a preferred choice for coatings due to its strength and resistance to surface degradation as well as due to its aesthetic and sparkly visual appeal. Electrolytic method of deposition is selected when it is required to have some control over the crystallite size, surface morphology and orientation of Ni which in turn significantly affects surface related properties of the coatings. Conventionally, Ni coatings have been prepared using dc electrochemical methods⁴⁻⁷. More recently, use of pulse electrodeposition has become popular since it results in Ni coatings with refined grain structure^{8,9} and attractive corrosion¹⁰⁻¹² and tribological properties¹³⁻¹⁸. Pulse plating is undertaken when current is applied in repetitive (pulse on - pulse off) square wave fashion rather than continuously as in dc plating. During pulse electrodeposition, peak current density, pulse on-time and pulse off-time are accurately controlled. Advantages of pulse electrodeposition include its cost effectiveness and high current density, power and range of pulse waveforms available for plating¹⁹. Pulse electrodeposition results in fine nanostructured coatings which show improvement in properties such as hardness, wear, abrasion, coefficients of friction, etc, compared to those produced by conventional dc plating.

Study of the corrosion behavior of nanostructured coatings is of considerable interest due its potential use as protective coatings in wide ranging applications. Fine grain

structure of nanocoatings results in high volume fraction of intergranular defects due to increased density of grain boundaries and triple junctions. There is a concern that this might have an adverse effect on the localized corrosion behavior of nanocoatings. However, previous studies have shown that Ni based nanocoatings are resistant to corrosion. Some studies report an improvement in corrosion resistance^{6,11,12} while others show behavior comparable to polycrystalline Ni¹⁰. It has also been reported that nanocrystalline Ni exhibited active-passive-transpassive polarization characteristics similar to coarse-grained polycrystalline Ni⁵⁻⁶.

In the present study, carbon steel samples were treated with sodium dihydrogen orthophosphate NaH₂PO₄.H₂O inhibitor prior to Ni electrodeposition. The authors have prior experience with the selected inhibitor because of its efficacy and excellent performance for protecting mild steel exposed to outdoor atmospheric environment²⁰. Our aim was to develop an active inhibitor layer underneath Ni that would provide added protection from corrosion. The idea was to combine beneficial effects of both nanostructured Ni coatings and that of the inhibitor resulting in an enhanced and long-term protection against corrosion. The effect of inhibitor on the adherence of Ni coating to the substrate was evaluated. Deposition of Ni was undertaken in Watt's bath using both dc and pulse electrodeposition techniques. Corrosion behavior of Ni coatings as well as inhibited plain carbon steel substrates was studied using Tafel potentiodynamic polarization technique in 3.5 wt% NaCl solution. Materials characterization was carried out using

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field emission scanning electron microscopy, cross-sectional scanning transmission electron microscopy, atomic force microscopy, X-ray diffraction and nanoindentation hardness tests. Role of microstructure on the corrosion properties of Ni coatings was examined.

2. Experimental

2.1. Electrodeposition

Plain carbon steel discs with 16 mm diameter were metallographically ground and polished to 1 μm surface finish. They were degreased with acetone and rinsed with distilled water. The composition of Watt's bath used for this study was NiSO₄.6H₂O (250 gm), NiCl₂.6H₂O (50 gm) and H₃BO₃ (35 gm) per liter of distilled water. Pure Ni sheet was used as anode and carbon steel as cathode during electrodeposition. The pH and temperature of the electrolyte was kept at 3.6 and 45 °C, respectively. A current density of 50 mA/cm² was used for dc plating. Pulse electrodeposition was performed at different peak currents of 5 A for durations of 20 minutes. Pulse on-time (Ton) and off-time (Toff) were set at 2 and 10 msec, respectively. Triplicate tests were run for each plating technique used for the present study.

2.2. Materials characterization

Atomic force microscope (AFM-contact mode, Agilent 5500 model) and field emission scanning electron microscope (FE-SEM, FEI NOVA NANOSEM 210 model) equipped with scanning transmission electron microscope (STEM) detector (attached to FEI Helios NanoLab) was used to examine the surface morphology and microstructure of electrodeposited Ni. The interface between the substrate and the Ni coating was imaged after preparing a thin cross-sectional sample using focused ion beam (FIB) instrument model FEI Helios NanoLab. An X-ray diffractometer (XRD model Rigaku Ultima IV MPD) equipped with a monochromator was used to determine the phase constitution, grain size and texture of Ni coatings. The diffraction spectra were generated using CuK α radiation ($\lambda=1.54184 \text{ \AA}$) source operating at 40 kV and 40 mA. Phase identification was carried out using a Bragg-Brentano (BB) configuration with $\theta/2\theta$ scan axis.

Instrumented nanohardness measurements were undertaken using a Berkovich (three-sided pyramid) diamond nanoindenter which penetrated the sample at a load of 100 mN and load/unload speed of 200 mN/min. The indenter remained stationary for 30 seconds between each loading and unloading cycle. The nanohardness data was generated from the normal force versus penetration depth curves. A set of four indentations was acquired for each test. Nanoindentation hardness (HS) is measured as the resistance to permanent deformation or damage and is calculated as follows:

$$HS \text{ (Pascal)} = F_{\text{max}} / A_p \quad (1)$$

Where, F_{max} = maximum force (N)
 A_p = projected contact area (m²)

2.3. Corrosion measurements

Carbon steel substrates were immersed in 10 mM solution of NaH₂PO₄.H₂O (sodium dihydrogen orthophosphate) inhibitor for a period of 24 hours prior to Ni electrodeposition. It is noteworthy that 10 mM NaH₂PO₄.H₂O solution was found optimal in our earlier study²⁰. Corrosion tests were carried out in neutral 3.5% NaCl solution at 23 °C. Tafel potentiodynamic polarization curves were acquired for ± 250 mV potential range with respect to open circuit potential and at a slow scan rate of 0.166 mVs⁻¹. A three-electrode cell (EG&G K-44) was used for corrosion measurements. A standard saturated (with 4M KCl solution) calomel electrode (SCE) was used as reference and the carbon steel samples were employed as working electrodes, whereas the graphite rods were utilized as counter electrode. The tests were controlled through a standard potentiostat/galvanostat EG&G Model 263A connected to a computer having EG&G 352 SoftCorr-III Corrosion Measurement Software.

3. Results and Discussion

3.1. Characterization of electrodeposited Ni

Surface morphology of Ni obtained using dc electrodeposition revealed coarse compact pyramidal-shaped grains as shown in the SEM micrograph of Figure 1a. Maximum grain size observed was approximately 3 μm . Pulse electrodeposition produced fine equiaxed grains existing in the form of colonies that are separated by crevices as shown in Figure 1b. Fine surface morphology of pulse electrodeposited Ni was also revealed in the AFM image of Figure 1c (Z-scale = 1.89 μm). Bright field STEM cross-sectional image of the interface between the substrate and Ni coating for pulse electrodeposit sample is shown in Figure 1d. It is clear that the grain size of Ni coating is small, especially in the initial stages of the deposition where it can be as fine as ≈ 10 nm. The difference in grain morphology obtained by dc and pulse electrodeposition was also shown by a difference in their instrumented nanoindentation hardness. The instrumented nanohardness values of Ni coatings obtained by dc method was 2492 MPa (230 VHN) compared to 3384 MPa (313 VHN) for pulsed Ni coatings. Refinement in grain size is thought to be responsible for an increase in the hardness of pulse coatings¹⁵.

Carbon steel samples were dipped in NaH₂PO₄.H₂O inhibitor for 24 hours and the top surface was examined using SEM. Inhibitor was uniformly distributed over the surface and exhibited a spherical morphology as shown in Figure 2a. Microchemical analysis of the top surface using SEM/EDS (Figure 2b) showed the presence of Na, P and O from inhibitor and Fe from underlying carbon steel substrate. The inhibited carbon steel surfaces were deposited with Ni using dc and pulse plating techniques. Surface morphology of dc and pulse plated Ni covering inhibited carbon steel (CS) samples is shown in the SEM images of Figures 2c and 2d, respectively. Application of a uniform Ni coating was possible and the presence of inhibitor on steel surface did not seem to adversely affect the electrodeposition process.

x-ray diffraction spectrum obtained from the top surface of pulse Ni electrodeposited sample is shown in

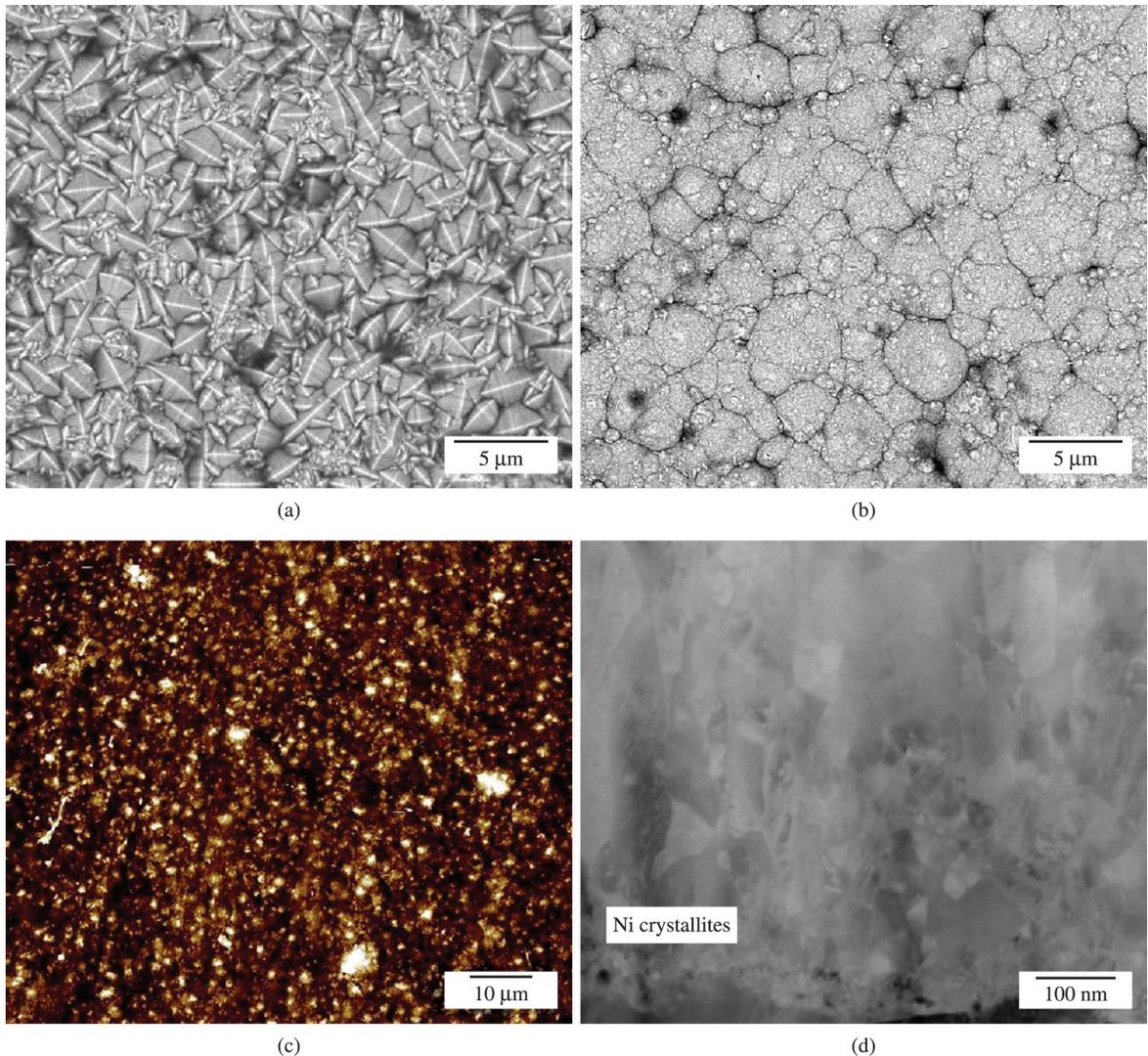


Figure 1. Surface morphologies of Ni produced by: (a) dc electrodeposition showing coarse pyramidal grains and (b) pulse electrodeposition showing fine equiaxed grains. (c) AFM (scale: $x=100$, $y=100$ and $z=1.89$ microns, step size 1.4 microns) and (d) Cross-sectional HAADF images of fine grained pulse Ni electrodeposit showing fine-grained structure. (HAADF – High Angle Annular Dark Field).

Figure 3. The peak with highest intensity corresponds to Ni (220) indicating preferred orientation. Preferred growth orientation of planes has been reported in literature for pulse deposited Ni^{9,13}.

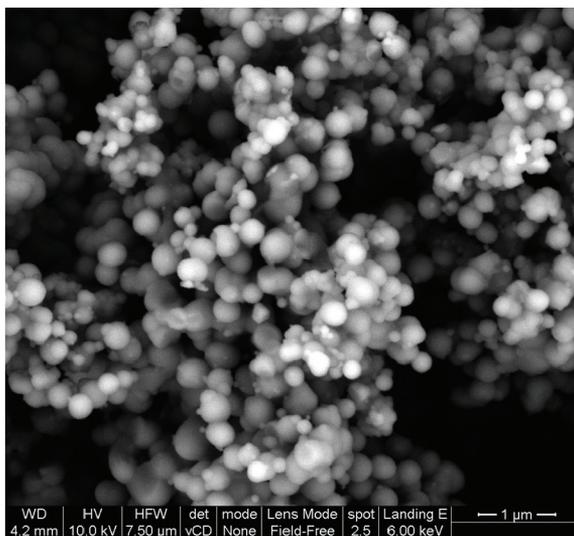
3.2. Corrosion measurements

The typical potentiodynamic polarization (Tafel) plots obtained for dc and pulse electrodeposited Ni with and without inhibitor treatments are shown in Figure 4 for the various electrochemical measurements listed in Table 1. As evident from the polarization curves of Figure 4, the zero current potential (ZCP) for treated fine grained Ni was comparatively more noble (positive) than that of untreated fine and coarse grained Ni. This is due to the fact that high grain boundary density in fine grained Ni influences the hydrogen evolution reaction shifting the potential to more noble values⁴. Also, the corrosion rate (CR) observed for

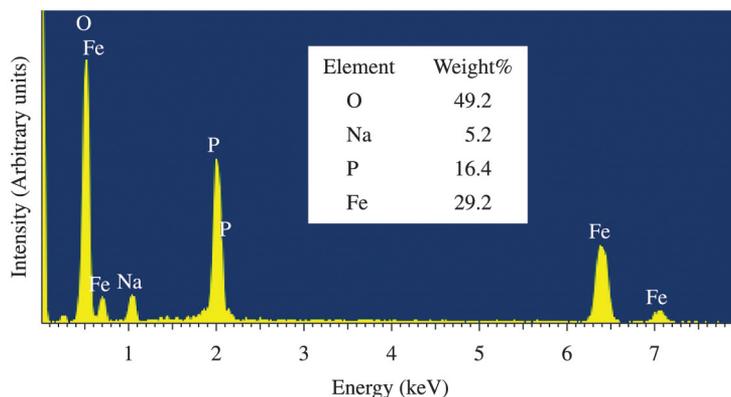
fine grained Ni was lower than its coarse grained counterpart (Table 1). This is attributed to more compact microstructure of fine grained Ni electrodeposit that results in an increase in the resistance to anodic dissolution^{5,12}.

The electrochemical behavior of inhibitor treated electrodeposits followed a pattern similar to that of untreated electrodeposits. Fine grained Ni exhibited nobler ZCP and lower corrosion rate compared to coarse grained Ni. A comparison between the polarization plots in Figure 4 reveals that electrodeposited Ni treated with inhibitor shows better corrosion properties than untreated Ni. Resistance to corrosion for coarse grained treated coatings is comparable for treated and untreated coatings. The overall corrosion behavior of all 4 types of electrodeposits can be rated from top to bottom (Figure 4) as:

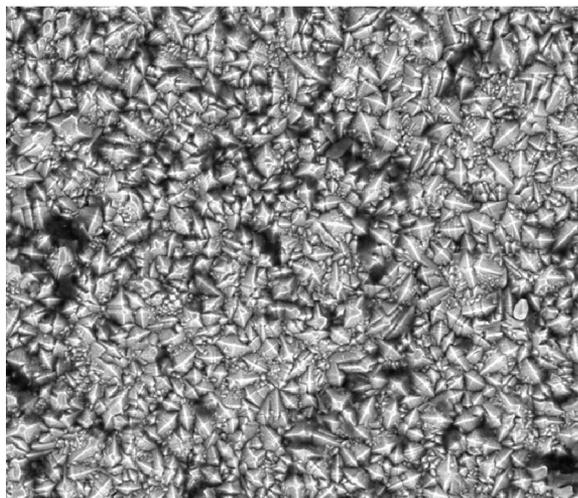
Treated fine-grain Ni (least CR) < Untreated fine-grain Ni < Untreated coarse-grain Ni < Treated coarse-grain Ni.



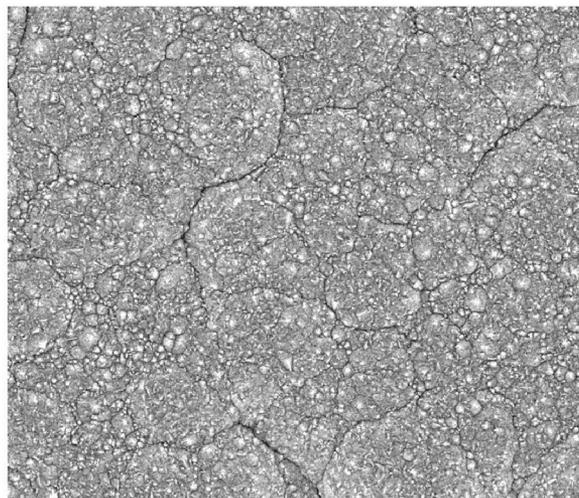
(a)



(b)



(c)



(d)

Figure 2. (a) SEM image and (b) EDS spectrum obtained from NaH₂PO₄.H₂O inhibitor. (c) Surface morphology of (c) dc and (d) pulse plated Ni covering inhibited carbon steel.

The corrosion rates observed in the present investigation, (Table 1), were not significant. Therefore, on the whole all the dc and pulse plated Ni coating remained within a range that can be classified as having low corrosion rates as corroborated well with the data found in the literature²¹.

3.3. Microstructure after polarization tests

Surface morphology of untreated coarse and fine Ni after polarization is shown in Figures 5a and 5b, respectively. Density and depth of pits in coarse grained Ni electrodeposit is higher. Pits are shallower and lower in density in

fine grained Ni. Surface morphology of coarse and fine electrodeposits treated with the selected inhibitor is shown in Figure 5c and 5d, respectively. Pit density is significantly lower in fine grained Ni. Surface damage of both treated samples is lower compared to that of untreated samples.

3.4. Role of inhibitor

The selected inhibitor, sodium dihydrogen orthophosphate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ is a film forming inorganic compound capable of retarding both cathodic and anodic reactions on the metals surfaces²². Based on our earlier

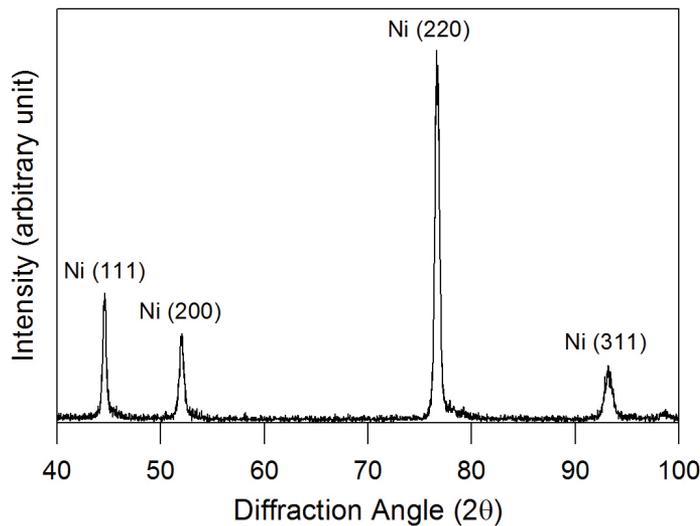


Figure 3. X-ray diffraction patterns XRD pattern obtained from pulse deposited Ni showing (220) preferred orientation.

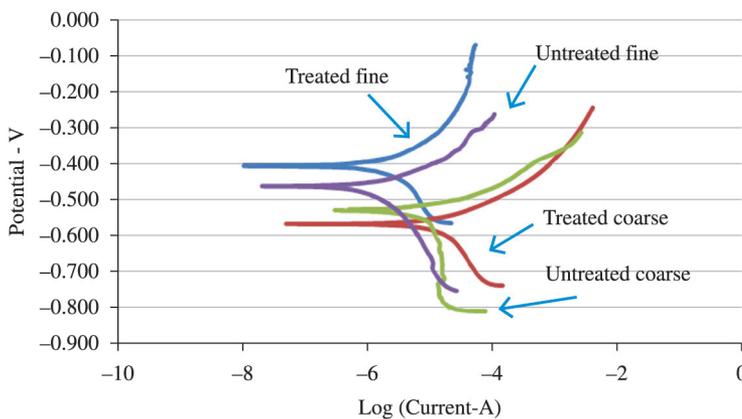


Figure 4. Potentiodynamic polarization (Tafel) plots obtained for coarse and fine Ni deposited on untreated and inhibitor treated carbon steel.

Table 1. Electrochemical measurements obtained from potentiodynamic polarization plots for untreated and inhibitor treated Ni electrodeposits.

	Untreated Ni (without inhibitor)		Treated Ni (with inhibitor)	
	Pulse (grain size <100 nm)	DC (grain size 3 μm)	Pulse (grain size <100 nm)	DC (grain size 3 μm)
ZCP, (mV)	-466.2	-523.5	-406.5	-569.1
Corrosion Rate (CR) - mpy	1.114	4.301	0.7026	4.554

mpy: mils per year, Tolerances: ZCP ± 15 mV, CR ± 0.5 mpy.

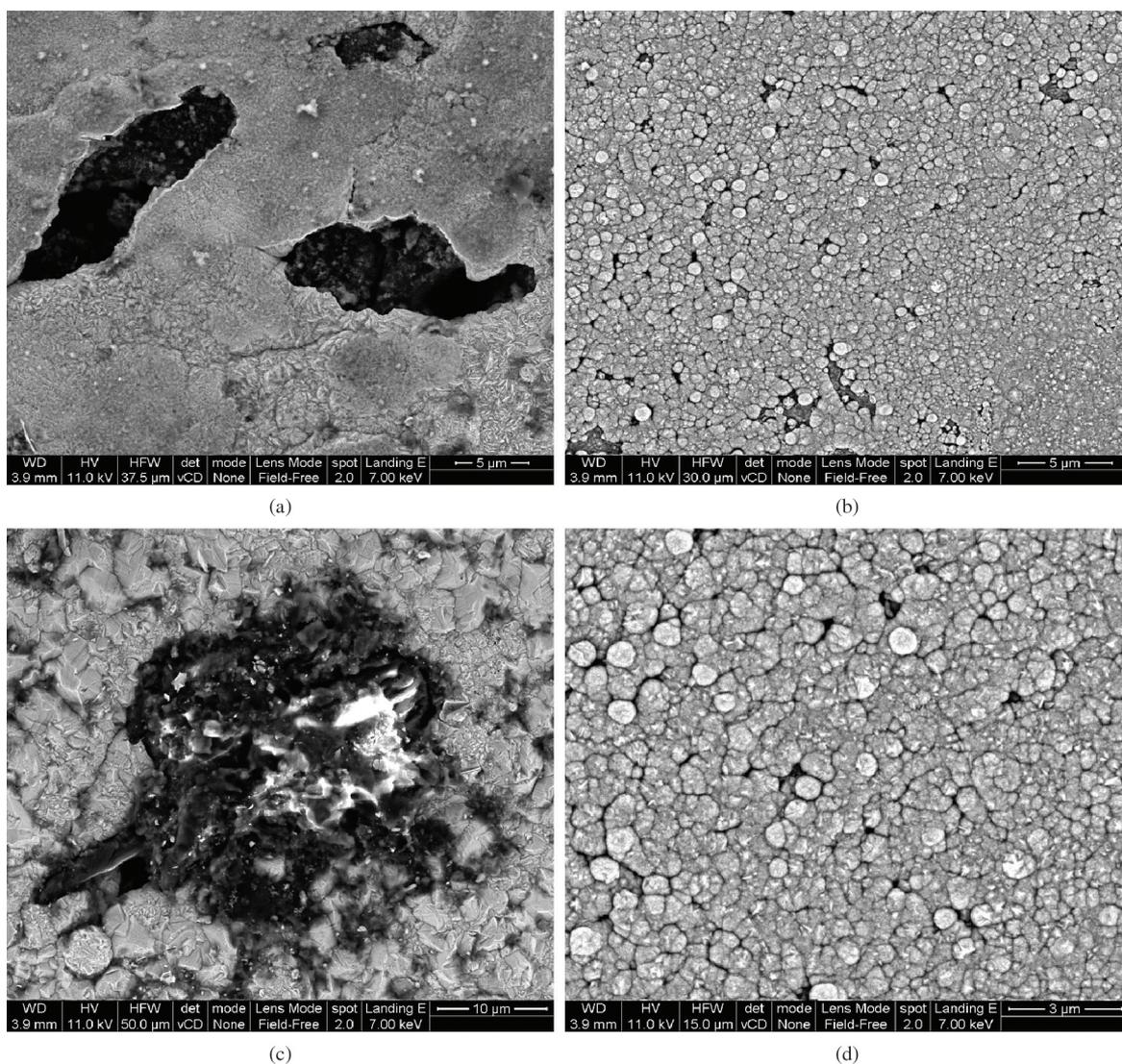


Figure 5. Surface morphology of Ni electrodeposit after polarization. (a) Coarse and (b) fine Ni on untreated carbon steel. (c) Coarse and (d) fine Ni on inhibitor-treated Ni.

experience, the inhibitor when used in 10 mM concentration had exhibited outstanding performance in protecting mild steel samples by showing the lowest corrosion rate of treated steel samples upto 180 days, in both electrochemical and weight loss measurements, and preventing discoloration of treated samples upto 130 days of atmospheric exposure²⁰.

In the present study, inhibitor NaH₂PO₄.H₂O was applied to the surface of the steel substrate prior to inserting it into the Watt's bath for electrodeposition. It was observed that the presence of inhibitor film at the cathode surface did not adversely affect deposition process. Identical deposition parameters were used for treated and untreated samples and uniform, continuous and adherent deposit was obtained in each case. The inhibitor's role became important as the corrosion process progressed. Its incorporation was believed to retard anodic dissolution and enhance corrosion protection of underlying substrate by acting as a barrier layer between the coating and the substrate. Influence of grain

size on the corrosion behavior was prominent in this study since layer(s) of inhibitor existed underneath the Ni coating which acted as an impermeable shield against the ingress of corrosive chlorides into the treated plated samples during the polarization tests in 3.5 wt% NaCl solution.

4. Conclusions

The electrochemical and corrosion behavior of coarse and fine Ni electrodeposit treated with NaH₂PO₄.H₂O inhibitor were compared with that of untreated Ni of corresponding grain size in the reported study. The treated fine grained pulse plated Ni exhibited nobler zero current potential and lower corrosion rate than both treated and untreated Ni pulse and dc-coated samples. The corrosion behavior of treated fine-grained Ni electrodeposit was found to be better than the untreated fine-grained Ni. Moreover, the treated and untreated pulse plated Ni coated samples

performed better than that of dc Ni plated samples from corrosion standpoint. No significant corrosion damage was observed in any of the dc and pulse plated Ni coatings that were tested and the corrosion rates remained practically within a low range.

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