

Enhanced Corrosion Resistance of Fe 500 Steel Rebars via Electroless Ni–P–MWCNT Composite Coating

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Abstract

This paper examines the impact of adding the ideas of multi-walled carbon nanotubes (MWCNTs) in a Ni–P metal matrix coating to enhance the corrosion behavior of steel. This composite coating was produced by the electroless deposition method. X-ray diffraction (XRD) was used to determine structural characteristics and Vickers microhardness was used to measure mechanical behavior. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods were used to investigate the corrosion behavior of the uncoated steel and Ni–P coated and the MWCNT-reinforced Ni–P coated samples. The corrosion potentials of the bare steel, Ni–P coating and Ni–P–MWCNT composite coating were determined as -470 mV, -428 mV and -342 mV, respectively. The interferometry of MWCNT-incorporated coating was observed to inhibit the substrate by 26.82 % as compared to the bare substrate, but the Ni–P coating interferometry improved by 14.63 % as compared to the plain steel. The above findings clearly indicate that MWCNT reinforced Ni P composite coating has a better corrosion resistance than the plain Ni P coating, and Fe 500 steel substrate.

Keywords: MWCNT; Electroless deposition; Vickers microhardness; Electrochemical impedance spectroscopy; potentiodynamic polarization.

1. Introduction

Steel is among the most common engineering materials used since it is cheaply produced; it has high carried capacity and high mechanical strength and thus remains an essential part of drilling equipment, pipes, marine, shipbuilding and offshore infrastructure. In spite of these merits, steel is most susceptible to corrosion especially in aggressive oilfield and marine conditions which have high temperature, high pressure as well as the presence of chloride rich and chemically reactive species [1]. The cost of such degradation is also very high, and there is a need to develop effective protection measures.

Nanomaterials have gained a lot of scientific and industrial interest over the past decades due to their wide range of applications in electronics, textiles, structural material, protective coating, renewable energy systems, agriculture, environmental remediation and biomedical technologies [2-4]. Their functional superiority is due to inherent nanoscale characteristics, namely, a very high surface-to-volume ratio, tunable surface chemistry, inexpensive synthesis pathways, and high catalysis activity. These properties allow a better control of reaction, effective transfer of mass and energy, targeted therapy delivery and enhanced surface engineering [5-9]. Nanomaterial-based coating has become one of the most efficient methods in reducing corrosion in metallic systems by surface modification.

Multi-Walled Carbon Nanotubes (MWCNTs) are some of the most appealing nanofillers in improving the corrosion behavior of Thermo-Mechanically Treated (TMT) steel rebars. Carbon nanotubes are known to have excellent mechanical and physical production characteristics such as high tensile strength (about 60 GPa), high Young's modulus (about 1 TPa), low density and high thermal conductivity [10]. Their exceptional rigidity and strength are as a result of the sp^2 hybridized carbon/carbon bonds in the graphitic lattice arrangement. These properties render MWCNTs very appropriate in terms of reinforcement factors in protective composite coatings [11].

Deterioration of steel, induced by corrosion in exposed structural components, in reinforced concrete systems, is one of the major causes of loss in durability [12, 13]. In reinforced concrete the initiation and propagation of corrosion is controlled by factors like moisture ingress, availability of oxygen, chloride penetration, concrete quality and thickness of the reinforcement cover. These include, among others, chloride attack, which is much more severe as compared to corrosion caused by carbonation [14]. A decrease in cross-sectional area and bond strength can significantly impair structural integrity over a period of time although the actual deterioration can take several years to manifest itself. Surface engineering strategies themselves can offer a feasible answer to the establishment of long-term durability through their methods.

It is worth noting that Electroless nickel (Ni-P) finishes have been adopted as a useful method of corrosion-protection because they offer a uniform thickness, high adhesion, excellent wear resistance, good ductility and excellent corrosion protection than conventional nickel electroplated finishes [15]. The autocatalytic deposition process guarantees a uniform coating to complex geometries. In an effort to further increase performance, several composite Ni-P coating that incorporate ceramic and solid lubricant particles are developed that exhibit better resistance to corrosion, wear, and abrasion on such materials like steel, aluminum, and copper. Although galvanization is still used in the reinforcement of steel via the control of corrosion, more effective and tunable corrosion protection is offered by the use of advanced composite coating.

The addition of carbon nano tube to Ni-P matrices was reported to improve hardness, wear resistance and corrosion characteristics of composite coating [16, 17]. It is possible that the presence of CNTs helps to create a stable passive coating and optimizes the microstructure of the deposit, which means less porosity and better barrier properties. Nonetheless, explicit studies of the mechanistic effect of doped CNTs in electroless Ni-P baths especially with TMT steel rebars are very few [18, 19]. Past research has revealed that the bath conditions including the constant stirring rate of 300 rpm and the use of complexing agents including lactic, succinic, and citric acids are important in enhancing coating homogenization and corrosion resistance [20-23].

Thus, the current research aims at creating a MWCNT-integrated electroless Ni-P composite coating of corrosion protection of steel rebar. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods are systematically used to assess the corrosion performance of the coated samples in a 3.5 wt. solution of NaCl in water, which is one of the service environment simulators of chloride-rich conditions.

2. Materials and Methodology

2.1 Preparation of metal substrate

This investigation used steel reinforcement bars in the form of reinforcements in accordance with IS 1786:2008 requirements as stipulated by the Bureau of Indian Standards (BIS), and have a nominal

diameter of 8 mm. Before subjecting the surface-to-surface treatment, the native oxide scale that was on the Fe 500 surface was first abraded using every sheet. This was followed by the use of acetone to remove the remaining contamination by immersion of the specimens in acetone at a time of 1 minute. After the degreasing, a desmutting treatment was done by placing the samples in a solution of acid prepared by adding 70 percent of nitric acid (HNO₃) to distilled water in the proportions of 1:5 and leaving the samples in the solution of acid solution. It was followed by alkaline conditioning of the cleaned substrates in a solution of 60 g/L sodium hydroxide (NaOH) dissolved in distilled water. The same process was performed at 60 °C with a continuous magnetic stirring speed of 400 rpm in 10 minutes time to attain a consistent surface activation process. Fig. 1 illustrates schematically the preparation of metal substrates.

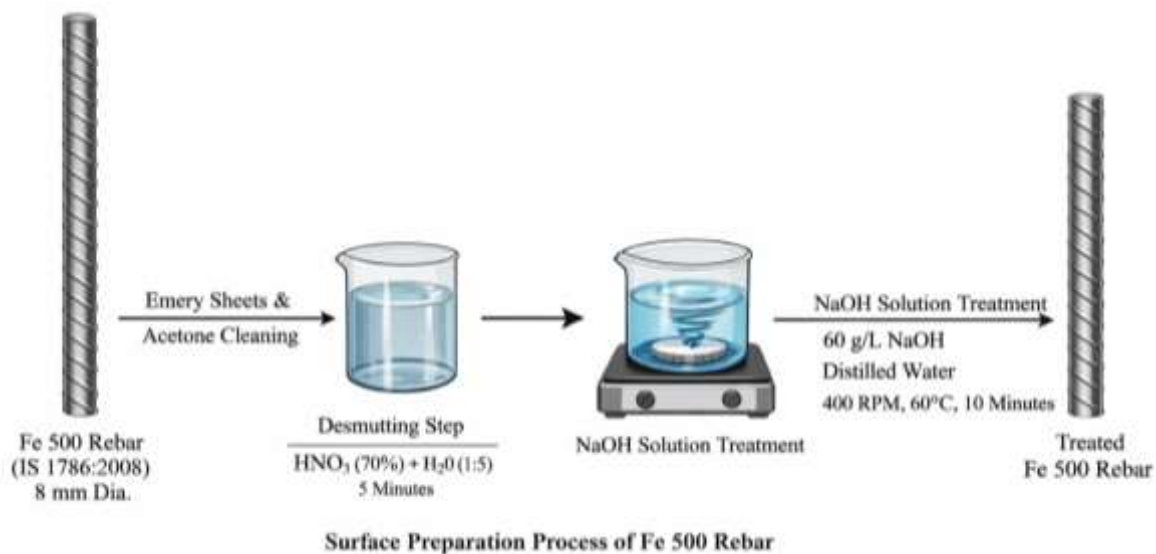


Figure 1: Schematic representation of Preparation of metal substrate

2.2 Preparation of Ni–P bath

A typical electroless plating bath consists of deionized water, a metal ion source, a reducing agent, complexing agents, stabilizers, buffers and wetting agents to achieve a uniform deposition. In the current system, nickel sulfate will serve as the source of Ni²⁺ ions, and sodium hypophosphite will serve as the reducing agent that leads to the autocatalytic process of producing the Ni P alloy coating. Complexing agents are introduced into the solution as organic acids: citric acid, lactic acid, and succinic acid, to control the free nickel ions at hand in the solution and stabilize the bath chemistry. The electrolyte pH is managed very carefully with the help of sulfuric acid and sodium hydroxide in order to preserve the conditions of preferred deposition. Kumar et al. (2023) [24] concluded that the agitation rate is the determinant of the quality of coating and the stirring rate is optimized at 300 rpm, which facilitates the achievement of higher coating uniformity and efficacy. They also observed in their study that addition of complexing agents like citric, lactic and succinic acids improves the mechanical properties and corrosion resistance of thermomechanically treated (TMT) steel rebars. A 200 mL bath volume will be used in the deposition process. First, the nickel salt, reducing agent and pH modifiers are used to form a Ni -P coating. After that, a coating of Ni-P-CNTS is formed through the addition of the necessary amounts of other complex elements and carbon nanotubes to the bath, as illustrated in Fig. 2.

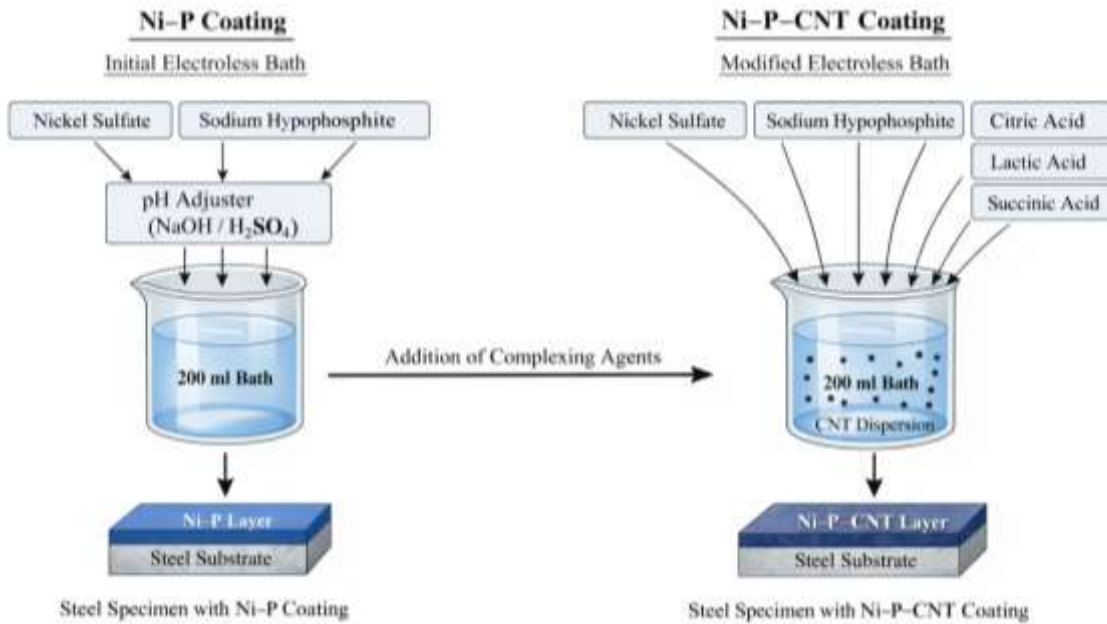


Figure 2: Schematic representation of preparation of Ni-P bath

3. Results and Discussions

3.1 XRD

Fig. 3 shows the XRD plot for the substrate that is coated with Ni-P and doped with CNT. The XRD plot for Ni-P reveals that there is a broad diffraction peak located in the 2θ range of $40\text{--}50^\circ$. This suggests that the Ni-P-coated sample is in an amorphous state [25]. The high percentage of phosphorus atoms causes the lattice to bend and strengthens it, which leads to the nickel crystalline structure becoming amorphous [26]. In the case of the MWCNT-doped coating, the peak is found at around $2\theta \sim 40^\circ$, but its intensity is lower compared to the Ni-P coated samples because of the presence of MWCNT nanoparticles.

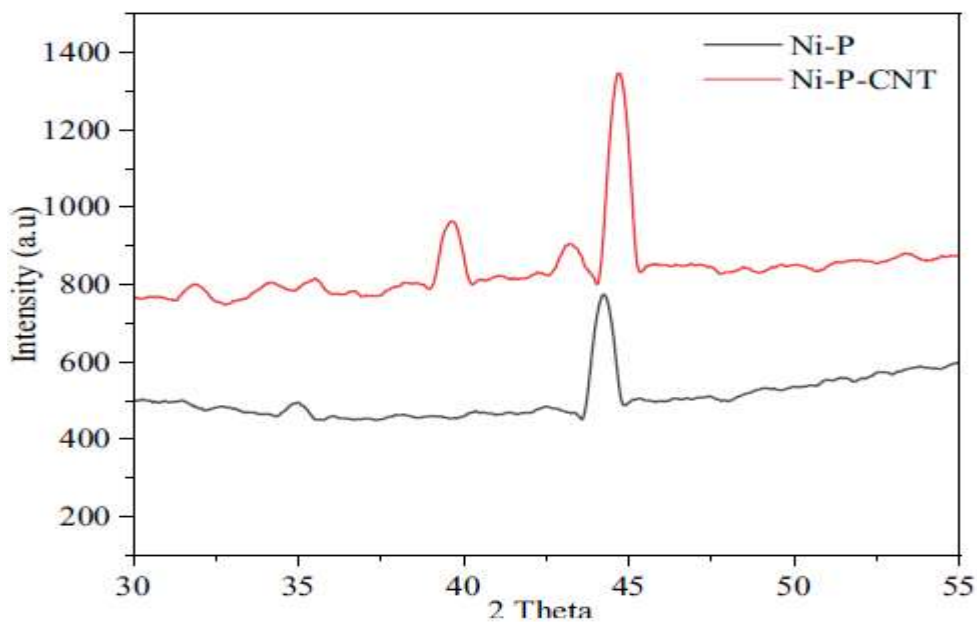


Fig 3. The XRD curve of the Ni-P coated substrate and CNT doped coated specimen

3.2 Microhardness of EN Coating

Vickers microhardness of uncoated and coated substrates was determined with the help of an Economet VH-1 MD hardness tester in 1002000 HV ranges and the data were represented in Fig. 4. A load of 0.2 kgf was used in each specimen over 10 s dwell time to provide the same indentation conditions. Through Fig. 4, the value of hardness in Fe-500 substrate was found to be 455 HV, but in electroless Ni-P coated sample, the value of hardness is 580 HV. Another improvement was noted on the CNT-integrated Ni -P coating that attained about 810 HV. This great enhancement in surface hardness of the Ni-P-CNT coated rebar can be explained by the synergistic effect of nickel-phosphorus matrix and uniformly distributed carbon nanotubes which are reinforcing agents and inhibitors of localized plastic deformation. Yang et al. [27] have also reported similar trends and attempted to determine the impact of single-walled carbon nanotube (SWNT) addition on hardness of Ni-P coatings and found that a higher temperature of annealing also increased the hardness values. The increased hardness developed in the CNT reinforced coating signifies wear resistance as well as increase in the durability of the surface against damage. Besides, the addition of multiwalled carbon nanotubes is effective towards the transfer of loads and microstructural refinement, leading to high microhardness levels than undoped Ni-P layer.

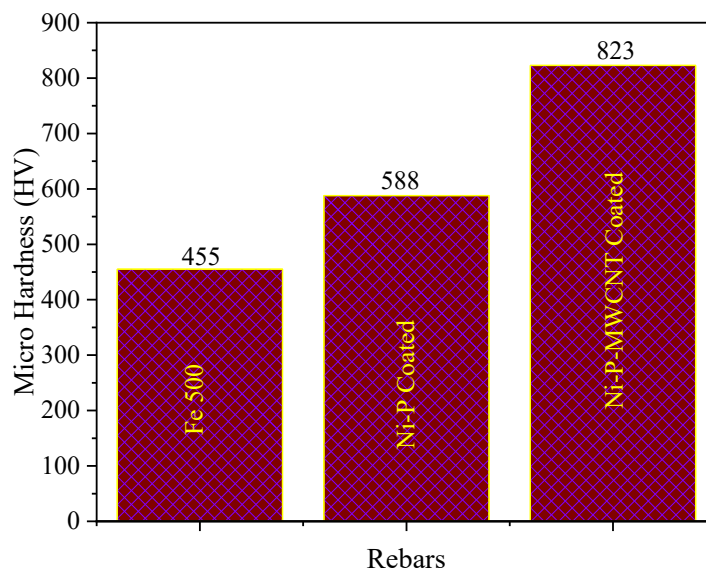


Fig. 4: Surface microhardness value of Bare, Ni-P and CNT-doped coated TMT steel rebar

3.3 Electrochemical measurements

3.3.1 Potentiodynamic polarisation method (Tafel plot)

The potentiodynamic polarization behavior of uncoated rebar and coated rebar composite in a 3.5 wt% aqueous NaCl solution is illustrated in Fig. 5 as a Tafel plot. The corrosion parameters, including E_{corr} , I_{corr} , β_c , β_a , and protection efficiency, are derived from the Tafel polarization curve, which is presented in Table 4.

The corrosion current densities (I_{corr}) values obtained from the Tafel plots are utilized to assess the protection efficiency (%) of the coating, which can be calculated using the following equation

$$(Protection\ efficiency) = \frac{I_c(i)}{I_c(o)} \times 100$$

$I_{corr}(o)$ are the bare substrate current densities and $I_{corr}(i)$ are the coated substrate current densities.

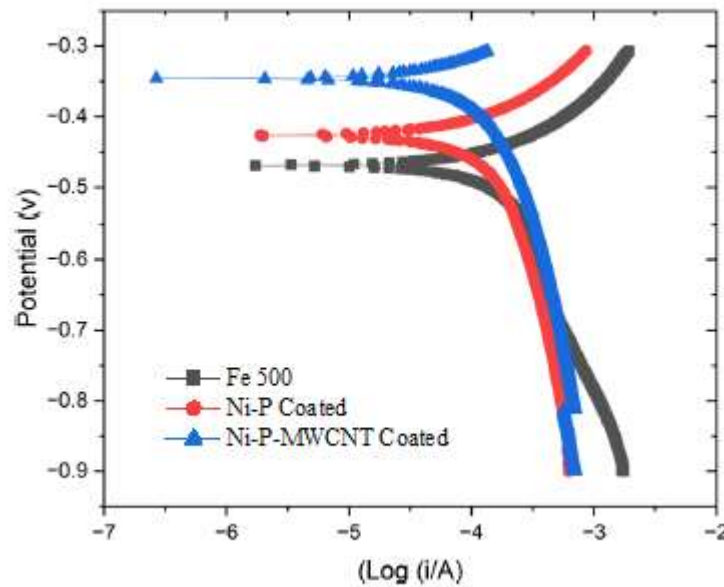


Fig. 5: Tafel polarization curves of an uncoated and coated substrate of the coating in 3.5% NaCl solution

Table 1 shows that addition of carbon nanotubes (CNTs) to the Ni P matrix boosts considerably the corrosion resistance of the sample as compared to the uncoated rebar and the traditional Ni P coated sample. When CNTs are in the electroless bath this causes a shift in the corrosion potential (E_{corr}) of the bath to more noble values and at the same time to a lower value in the corrosion current density (I_{corr}), meaning an enhanced electrochemical stability. Additionally, the CNTs alter the Tafel behavior, which leads to a relatively lower cathodic Tafel slope and a more pronounced anodic slope. The low β_c indicates a faster cathodic reaction that can be explained by the nature of the low hydrogen overpotential of CNTs that enables hydrogen evolution. Moreover, the ternary NiP CNT coating has more phosphorus content than the binary NiP layer, which is associated with the positive shift in the corrosion potential, which is probably caused by a partial replacement of nickel by MWCNTs within the composite structure [28]. Consequently, the CNT reinforced coating has a protection efficiency nearly 26.5 times higher than the uncoated substrate and the Ni P coating without CNTs has an enhancement of almost 14.6 times when compared to the uncoated rebar.

Table 1: Corrosion resistance of doped CNT coatings is improved compared to both Ni–P coated rebar and bare rebar.

Coating	E_{corr} (mV)	I_{corr} (μAcm^{-2})	β_c	β_a	Protection Efficiency (%)
Fe 500	-0.470	4.438	-0.921	0.191	0
Ni-P coating	-0.428	3.789	-0.456	0.157	14.63
Ni-P-MWCNT Coating	-0.342	3.182	-0.253	0.071	26.82

3.3.2 Electrochemical impedance spectroscopy (Nyquist plot)

The Nyquist plot that fits the EIS curve helps to further explore corrosion behavior, as shown in Fig. 6. The Electrochemical impedance measurements, which include solution resistance (R_s), charge transfer

resistance (R_{ct}), and double layer capacitance (C_{dl}) was determined. The different parameters obtained from the Nyquist plot are determined using Z-View software.

The corrosion inhibition efficiency was calculated by comparing the charge transfer resistance using the following equation

$$(\text{Corrosion inhibition efficiency}) = 1 - \frac{R_{ct}(i)}{R_{ct}(o)} \times 100$$

where $R_{ct}(o)$ represents the charge transfer resistance of the bare substrate and $R_{ct}(i)$ indicates the current densities of the coated substrate. An electrochemical impedance fitting showed that there was a notable enhancement in the corrosion resistance after the surface modification. R_{ct} of the uncoated substrate was about $17.86 \text{ k} \Omega \text{ cm}^2$. This value was approximately $19.57 \text{ k} \Omega \text{ cm}^2$ with the Ni-P coated sample and was further escalated to approximately $24.29 \text{ k} \Omega \text{ cm}^2$ when CNTs were added to Ni-P matrix. The potential inhibition efficiency of corrosion was determined to increase by a percentage of 9.57 of the Ni-P coating over the bare substrate but the Ni-P-CNT coating had much higher efficiency of 24.49%. The gradual rise in R_{ct} value affirms the fact that the composite coating is a more effective protection in respect to corrosion-related processes of charge transfer.

Furthermore, the values of the double layer capacitance (C_{dl}) reduced post coating, which is a sign of a reduced area of electrochemically active surface resulting in better protection. The same trends have been observed in previous research work whereby C_{dl} values have been found to reduce with addition of SiC to Ni-P coatings by 37.51 to $36.66 \mu\text{s}\Omega^{-1} \text{ cm}^{-2}$ and the R_{ct} increased by 18.45 to $31.32 \text{ k} \Omega \text{ cm}^2$. Similarly, the inclusion of SiO_2 particles into Ni-P coating lowered C_{dl} to $17.12 \mu\text{s}\Omega^{-1} \text{ cm}^{-2}$ to $26.92 \mu\text{s}\Omega^{-1} \text{ cm}^{-2}$ and R_{ct} to 5.02 n to $4.12 \text{ k} \Omega \text{ cm}^2$. These results repeatedly prove that barrier properties and general corrosion resistance are increased as reinforcing nanoparticles are incorporated into the Ni-P matrix.

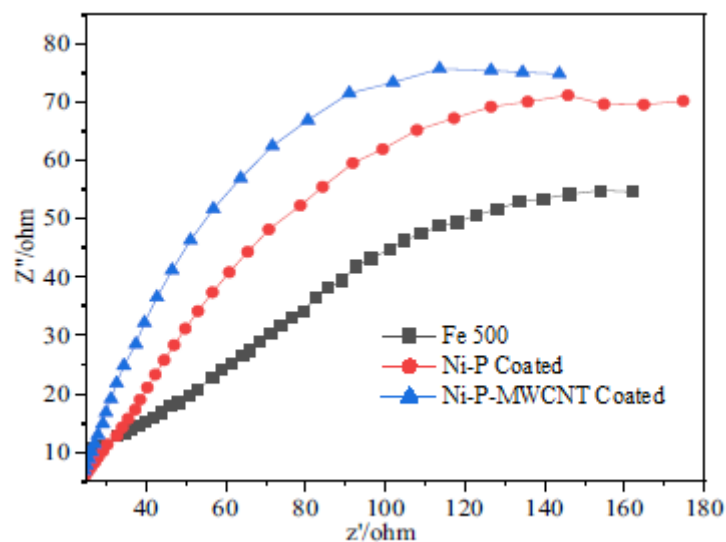


Fig. 6: Nyquist plots for fitting curves for bare and coated substrates in 3.5 wt% of aqueous solution

MWCNT helps reduce surface and structural imperfections by filling in coating gaps and tiny pores. As a result, integrating CNT into the Ni-P matrix leads to a denser and more consistent coating. A large

semi-circular loop is seen in the Nyquist plot for the Ni–P–CNT coating on rebar, which indicates strong corrosion resistance, as illustrated in Fig. 6. The curves for both the bare rebar and the coated rebar form a single semicircle in the high-frequency range. The addition of CNT nanoparticles changes the microstructure of the Ni–P layer, creating a composite coating that offers better corrosion resistance than plain steel rebar. Phosphorus plays a crucial role in enhancing the coating's corrosion resistance, significantly affecting its structure.

4. Conclusions

The current study has shown that the addition of the multi-walled carbon nanotubes (MWCNTs) to an electroless Fe 500 steel rebar through incorporation into an electroless Ni -P matrix greatly improves the surface and corrosion properties of Fe 500 steel rebar. The amorphous nature of the Ni–P coating was verified through structural analysis and the microhardness of the sample showed a significant enhancement in the hardness of the bare substrate to the CNT-reinforced composite layer as a result of successful dispersion strengthening and microstructural refinement. Electrochemical investigations on 3.5 wt.% NaCl solution revealed a significant positive shift of corrosion potential and a decrease of the densities of corrosion current in the case of Ni-P-MWCNT coating, which indicated better corrosion resistance than in the case of uncoated sample and plain Ni-P coated sample. The increased amount of charge transfer resistance and decreased double layer capacitance also confirm the growth of a dense protective barrier layer. Altogether, the pioneered Ni-P-MWCNT composite coating is a viable and effective way forward in improving the durability and service life of steel reinforcements in deforming chloride conditions.

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