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**Structural Characterization and Corrosion Properties of Electroless
Processed Ni–P–MnO₂ Composite Coatings on SAE 1015 Steel for Advanced
Application**

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Abstract

In recent year electroless Ni-P coatings with the incorporation of metallic oxides have received profound interest due to their unique properties and ability to enhance the operational performance of the based metal. These coatings have been utilised for numerous applications such as aerospace, automotive and industrial field where materials with exceptional qualities are required. This present work focused on the improvement of the surface characteristics of mild steel via the electroless deposition of Ni-P-MnO₂. The deposition was achieved varying the mass concentration of MnO₂ at a constant temperature and deposition time of 85 °C and 20 minutes respectively. The examinations of the coated surfaces using Scanning Electron Microscope revealed that the surface morphology of the coated steel improved as the mass concentration of MnO₂ increases. Linear potentiodynamic polarization experiment unveiled that Ni-P-MnO₂ coating exhibits good corrosion resistance, protecting the steel from the penetration of corrosive ions in the test medium. Moreso, the investigation of the microhardness behaviour of the coated samples using the Vickers hardness tester shows that Ni-P-MnO₂ coating enhanced the microhardness of the steel substrate.

Key words: Electroless; Coating; Morphology; Corrosion and Hardness.

1. Introduction

The durability and applicability of material is decided by its surface properties. To achieve superior performance, physical or chemical modification of surfaces is inevitable. Surface modifications have been largely used as a benchmark for various applications so as to enhance properties and advanced functionalities of materials [1]. Ni-P electroless deposition has been considered a vital surface engineering technology with multifunctional industrial applications. Embedding composite nanoparticles in electroless deposited Ni-P is a convenient strategy of attaining optimal deposition and enhanced performance characteristics [2].

Ni-P has been co-deposited with different types of second-phase nanoparticles to enhance mechanical, electrical, magnetic and electrochemical properties of metals [3, 4]. The remarkable hardness and exceptional corrosion resistance ability of electroless Ni-P thin films account for their deposition on metal surfaces [5]. Moreso, irregular shaped surfaces and substrates of aluminium, steel, plastic and glasses have been coated via electroless

deposits of low porosity [6]. The particulate content in Ni-P matrix and the properties incorporated in the composite deposits are functions of the shape, size, type of particle and plating bath conditions such as pH, stirring rate and temperature [7-9]. Electroless Ni coating, unlike electrodeposition, is an autocatalytic reaction where electricity or passage of current through the plating solution is not required for homogeneous deposition [10, 11]. Good dispersion of particles can be achieved by maintaining the particles suspension in the solution via vigorous agitation. However, it is quite difficult to achieve adequate suspension of particles because of the large surface area. The high surface energy results in the agglomeration of particles during the coating process, although some other factors might lower the agglomeration tendency [12, 13].

More so, the choice of the embedded nanocomposite particles in Ni-P electroless coating is significant. The inherent properties of the particles are important factors that must be put into consideration. The notable improvement in properties has been recorded by several investigators having co-deposited particles such as Al_2O_3 , SiO_2 , SiC and MoS_2 in binary Ni-P alloy [14]. Improvement in properties of Ni-P electroless coatings has widened its application. This present work investigates the effect of incorporation of MnO_2 particles and MnO_2 concentration on the anti-corrosion properties of Ni-P and Ni-P- MnO_2 on mild steel in 3.5 % NaCl solution via linear potentiodynamic polarization techniques. The microhardness of the samples was determined using Vickers hardness techniques. SEM was used to investigate the morphology of the samples. The coated steel can be utilized in various applications such as aerospace, automotive and marine.

2. Experimental Procedure

2.1. Sample Preparation

Mild steel and all the chemicals used for this experiment were purchased in South Africa. The mild steel was cut into coupon of dimension 40 mm x 40 mm x 2 mm and 99.9 % Nickel plate of 50 mm x 40 mm x 10 mm. Table 1 shows the steel's chemical composition. The samples were polished and cleaned via immersion in 0.01 M of Na_2CO_3 solution at a room temperature of 25 °C for about 10 s. The samples were pickled and activated using 10 % HCl for 10 s at room temperature and this was closely followed by quick rinsing in deionized water.

Table 1. Composition of mild steel in wt. %

Element	Mn	C	S	Si	P	Ni	Al	Fe
Composition	0.44	0.15	0.032	0.17	0.01	0.009	0.006	99.183

2.2. Coating Bath Preparation

Four different baths were prepared varying the mass composition of MnO_2 . All reagents and particulates were dissolved in deionized water and left for 48 hours maintaining a pH value of 5.5. The bath was heated to 85 °C and stirred using magnetic stirrer for better dissolution. **The Composition** of the bath prepared is shown in Table 2.

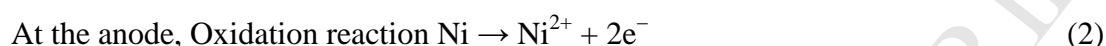
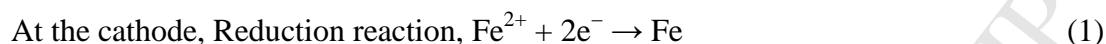
Table 2. Bath composition and Operating conditions

Composition	Mass concentration(g/L)
Nickel chloride	75
Sodium hypophosphite	35
Sodium Chloride	45
Thiourea	5
Boric acid	10
MnO_2	0-15
Operating conditions	
pH	5.5
Time	30 mins
Temp.	85 °C

2.3. Electroless Plating of Ni-P and Ni-P- MnO_2

The bath prepared was continuously stirred at 250 rpm and a constant temperature of 85 °C during the deposition process to achieve suspension stability and minimize agglomeration of particles. Minimal agglomeration improves the electrophoresis mobility of the bath solution [15]. Stirring of the bath keeps the particles of Ni-P and Ni-P- MnO_2 suspended in the electrolyte bath and more so enables the mass transportation of the particles to the steel surface. Continuous agitation enhances the quantity of deposition of the particles on the steel surface. However, excessive agitation could affect electrodes stability; alter the transfer

region of the charges which might consequently lead to low-quality deposit on the steel surface [16]. During the electroless deposition process, the mild steel (cathode) was placed equidistance between two Ni plates. The distance between the steel (cathode) and Ni (anodes) was 3.2 cm. The deposition time, pH and temperature were kept constant varying the mass concentration of MnO_2 . In the course of the deposition, a lot of reactions occur. Eqn. 3 is the cell reactions between Ni and the base metal during the electroless deposition process.

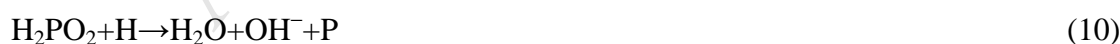


2.4. Mechanism of Electroless Ni-P Deposition Reaction

The electroless Ni-P deposition reaction mechanisms are yet to be well understood [17]. However, there are two widely acceptable reaction mechanisms [18]. The mechanisms are ‘‘Electrochemical mechanism’’ and ‘‘Atomic hydrogen mechanism’’. The electrochemical mechanism involves the catalytic oxidation of the hypophosphite to produce electrons at the catalytic surface which consequently minimises nickel and hydrogen ion as shown below:



The ‘‘Atomic hydrogen mechanism’’ involves the release of atomic hydrogen because the product of the catalytic hydrogenation of hypophosphite molecule adsorb at the surface as shown below;



The active hydrogen adsorbed reduces Ni at the catalyst surface.



2.5. Linear Potentiodynamic Polarization Test

The electrochemical test was carried out using the three-electrode cell in a 3.5 % NaCl solution. The corrosion behaviour of the samples was examined at a room temperature of 25 °C with the aid of the three-electrode cell. The graphite rod acted as the contact electrode, Ag/AgCl as the reference electrode and mild steel was the working electrode. Tafel curves were obtained from -2.5 V to 0.5 V at 0.005 m/s scan rate.

3. Results and Discussion

3.1. Potentiodynamic Polarization Test

Potentiodynamic polarization experiment carried out on Ni-P and Ni-P-MnO₂ electroless coated steel revealed their corrosion resistance ability in 3.5 % simulated NaCl solution. The corrosion test result was generated from the extrapolation of the polarization curve shown in Fig.1 which established the corrosion resistance improvement as the mass concentration of MnO₂ increases. The rate of corrosion of Ni-P coated sample was 4.6375 mm/year and this reduces drastically to 1.1871 mm/year for the Ni-P-15MnO₂ coated sample. It can also be seen in Table 3 that the Ni-P-15MnO₂ coated sample possesses the maximum polarization resistance of 113.93 Ω and the lowest current density of 0.003084 A/cm². This could be attributed to the adhesiveness, nature and chemical stability of the passive film generated by Ni-P-15MnO₂ on the surface of steel [19]. Generally, the low current densities of the Ni-P-MnO₂ samples are indication that addition of MnO₂ into the matrix of Ni-P offered more defence against the penetration of chloride ion at the active site of the steel. The barrier formed by the coating reduces the cathodic evolution and metal dissolution reactions at the anodic site of the steel [20, 21]. Generally the presence of Ni-P and Ni-P-MnO₂ in the steel matrix limits the concentration of chloride ion. This consequently lowers the density of current in the charge transfer controlled and mixed potential region.

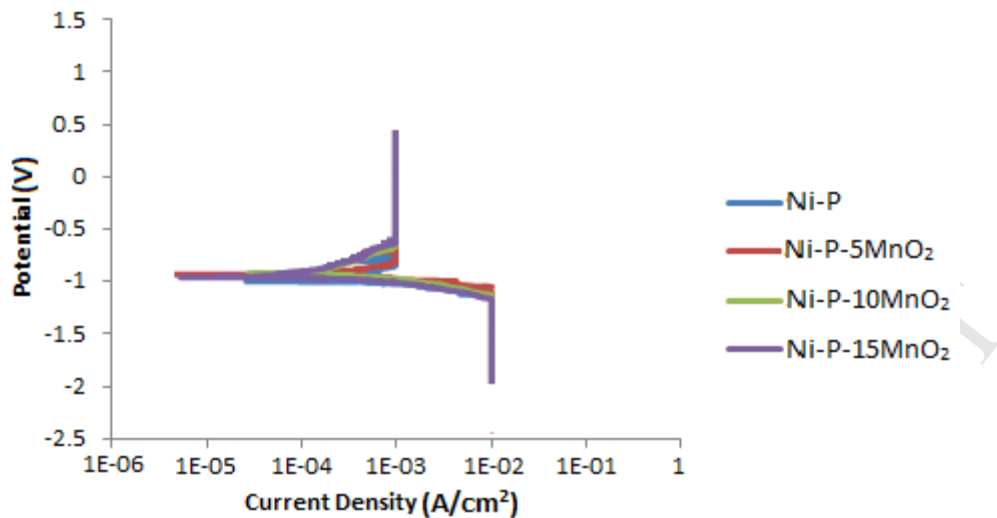


Fig.1: Potentiodynamic polarization curves of coated samples

The degree of charge transfer at the metal and liquid interface depends on the utilised potential and the mass of reacting species. The degree of the charge transfer effect at the interface depends not solely on the employed potential but also on the concentration of reacting species predominant at the metal surface [22]. The closed value of E_{corr} confirms the mixed inhibitive nature of the coating [23, 24].

Table 3: Potentiodynamic polarization data of samples

Samples	E_{corr} (V)	j_{corr} (A/cm ²)	Cr (mm/year)	Pr (Ω)
Ni-P	-0.98894	0.012033	4.6375	50.929
Ni-P-5MnO ₂	-0.96072	0.006406	2.4689	78.527
Ni-P-10MnO ₂	-0.92377	0.003798	1.4636	93.784
Ni-P-15MnO ₂	-0.92351	0.003084	1.1871	113.93

3.2. Surface morphologies of coated samples

Fig.2 (a-d) revealed the surface morphologies of Ni-P coating and Ni-P-MnO₂ composite coatings. The agglomeration of MnO₂ nano-particles and particles mixing can be seen clearly in Fig.2c and d. These were minimal in Fig.2b due to the low mass concentration of MnO₂. Fig.2a exhibits predominantly single clustered morphology with some pores. However, the cluster disappeared gradually on the inclusion of MnO₂. The presence of pores could be attributed to the formation of hydrogen at the surface of the Ni-P surface [25]. Generally, the porosity of the coated surfaces decreases as the mass concentration of MnO₂ increases. Fig.

2a and b showed typical flake structures while Fig. 2c and d are predominantly nodular structures with redefined morphology making it look smoother and more attractive.

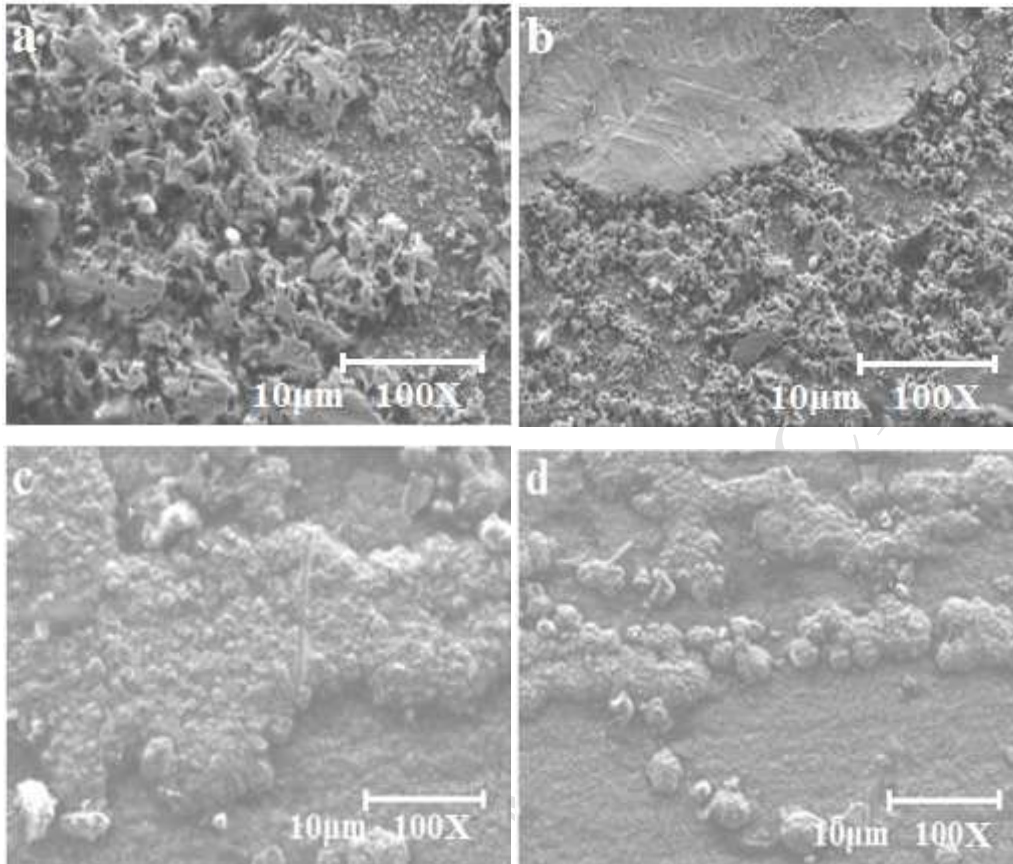


Fig.2 SEM micrograph of (a) Ni-P (b) Ni-P-5MnO₂ (c) Ni-P-10MnO₂ (d) Ni-P-15MnO₂ coated samples

3.3. Microhardness of Ni-P and Ni-P-MnO₂ Coated Samples

Fig.3 shows the microhardness result obtained for Ni-P and Ni-P-MnO₂ Coated Samples. The microhardness values were obtained using the Vickers hardness testing technique. The test was carried out in accordance with ASTM A-370 [26]. Ni-P coated sample was found to possess the lowest microhardness value of 125kgf/mm². Fig.3 revealed that the value of the microhardness of the samples increases as the mass concentration of MnO₂ increases. The Ni-P-15MnO₂ coated steel exhibit the highest value of 197 kgf/mm² which represents a 57.6 % increase in microhardness when compared to the microhardness value of Ni-P coated steel. The improvement in the microhardness value could be traceable to the development of adhesive mechanism by the Ni-P-15MnO₂ coating, strain energy in the boundary of the composited coated steel and bath processing parameters [27-29].

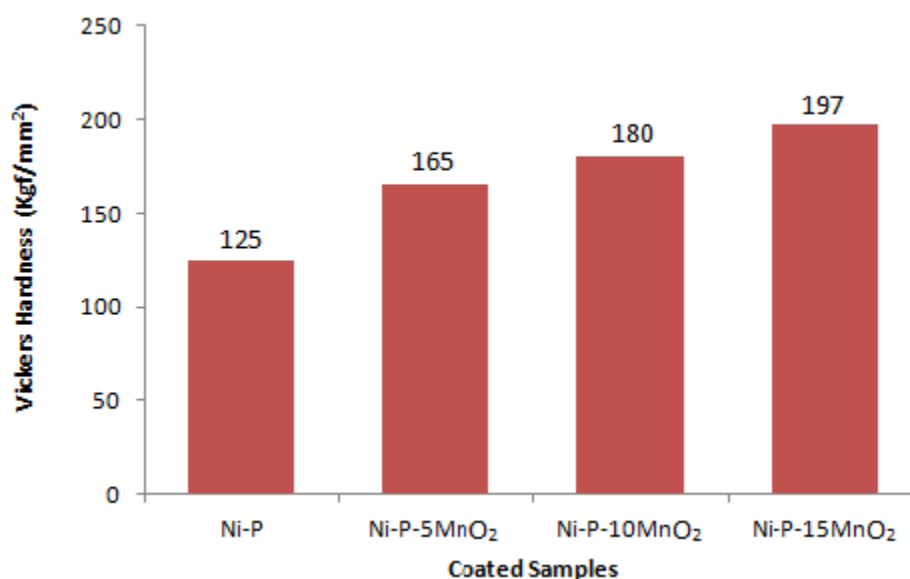


Fig. 3: Microhardness of Ni-P and Ni-P-MnO₂ Coated Samples

4. Conclusions

Ni-P and Ni-P-MnO₂ electroless coating were successfully produced. The particles of MnO₂ were discovered to have improved the corrosion resistance, microhardness and morphology of the Ni-P coated steel. The Ni-P-15MnO₂ coated sample exhibit the highest hardness value of 197 kgf/mm² which represents a 57.6 % increase in microhardness when compared to the microhardness value of Ni-P coated steel. The potentiodynamic polarization experiment shows that MnO₂ lowers the corrosion rate of the steel by limiting the ingress of chloride ion to the active site of the steel. Ni-P and Ni-P-MnO₂ behaved predominantly as a mixed inhibitor due the close values of the corrosion potentials.

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