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Performance Evaluation Effect of Nb_2O_5 Particulate on the Microstructural, Wear and Anti-corrosion Resistance of Zn–Nb_2O_5 Coatings on Mild Steel for Marine Application

T. Oluyori[1,2] · O. E. Olorunniwo[1] · O. S. I. Fayomi[3,4] · P. O. Atanda[1] · A. P. I. Popoola[4]

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Abstract In this study, we developed Zn–Nb_2O_5 composite coatings from sulfate bath for wear and corrosion performance on mild steel by electrodeposition technique. The effect of Nb_2O_5 particulate on the Zn–Nb_2O_5 properties was investigated. The particle volume fraction was varied within between 10 and 20 wt%. The structural properties of the composite coatings were characterized using scanning electron microscope equipped with energy-dispersive spectrometer. The hardness and wear of the composite coating were measured with diamond base microhardness indenter tester and sliding CETR reciprocating wear testers, respectively. The corrosion properties were examined in 3.65% NaCl using AUTOLAB 101 Metrohm potentiostat–galvanostat with linear polarization technique. The results showed that average hardness value of 192.6 and 200.6 HV and passivation potential of 4.39E+08 and 5.30E+08(Ω) were obtained for the 10–20 wt% Nb_2O_5 particulate on the Zn–Nb_2O_5 coatings. The wear performance improves by 63.4% as against the control sample. In all, this study established that up to 20 wt% of Nb_2O_5 in Zn–Nb_2O_5 composite coating significant corrosion, wear and microhardness propagation resistance of mild steel was attained.

Keywords Zn–Nb_2O_5 coatings · Nanocomposite · Microstructure · Corrosion · Wear

✉ O. S. I. Fayomi
ojosundayfayomi3@gmail.com

T. Oluyori
rtoluyori@gmail.com

[1] Department of Materials Science and Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria

[2] Department of Metallurgical Engineering, Kogi State Polytechnic, Lokoja, Nigeria

[3] Department of Mechanical Engineering, Covenant University, P.M.B. 1023, Ota, Ogun State, Nigeria

[4] Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa

1 Introduction

The challenges of mild steel in major engineering application are broadly classified into chemical and mechanical deformation [1]. The chemical influence often generate into corrosion degradation and the mechanical factors causes vital stress initial inform of wear plastic deformation and thermal instability at high temperature application [2, 3]. Effort has been made by several researchers to curtail this growing impact with several surface preventive measures like hot dipping, vapor deposition, cold spray and laser cladding to mention but a few. The limitation of these modification technique have been seen to gives rise to high cost value, high thin film precision with less durability [4]. Electrodeposition is a valuable technique used in most engineering industries for fabrication of special product for marine, photoelectronics, automobile, decorative and aerospace application [5, 6].

Zinc and nickel coating are common and versatile coating system for corrosion protection of steel [7]. The major limitation of zinc coating is its reduction characteristics at elevated temperature apart from pollution challenges associated with cyanide and acids solution. Another setback of ordinary zinc deposition is the challenge with robust bath frame work in relation to high cost incur when compared with sulfate and chloride bath [8]. However, several authors affirmed that excellent deposition depend on oxidation and reduction of metal ion, nature of bath

constituent, complexing agents, pH, time of immersion, strengthening agents and other vital ingredient.

Particulate in form of ceramics, composite and nanocomposite have also been attested to contribute maximally to the propagation and performance characteristics of bath for effective fabrication of coating [9–11]. In view of this, co-deposition reinforced metal matrix has been seen as a platform to provide suitable desired coating with target of service improvement. Many nanoscale materials are known to possess special properties that differ significantly from those exhibited in the bulk state. Nanocomposite materials have various unique properties, including excellent corrosion and wear resistance, resistance to high temperature oxidation, self-lubricity and so on [12, 13].

In addition, coating reinforced with ZrO_2, TiO_2, Al_2O_3 and SiC particulates into bath rich electrolyte often formed metal matrix composite coatings [14, 15]. Likewise, selected alloys and composites such as Zn–Ni, Zn–ZrO_2, Zn–TiO_2 and Ni–SiC are currently been developed as surface modified coating ahead of chromium coatings because of their brilliant performance and eco friendliness [16]. More so, detail of evolution and corrosion characteristics by researchers on Nb_2O_5 as an integrated particulate for composite strengthening via electrodeposition has not been explored.

Effort to obtain a more stable coating for improved service life with target on mechanical, wear and corrosion resistance has necessitated this study. Therefore the aim of this work is to prepare and electrodeposits Zn–Nb_2O_5 matrix coatings on mild steel substrates from a single sulfate electrolyte and hence obtained strong structural evolution, significant corrosion resistance and good wear characteristics.

2 Experimental Procedure

2.1 Materials Preparation and Co-deposition

Mild steel sheet (as-received substrate) with the dimensions 40 mm × 30 mm × 20 mm and zinc sheets anode 50 mm × 40 mm × 4 mm were commercialized sourced from Owode Onirin in Lagos Nigeria. The substrate was discalced and degreased according to criterion standard attested by [11]. The chemical compositions of the mild steel specimens after spectroscopy analysis were presented in Table 1. The cathode was a mild steel sheet and the anode was pure zinc with (99.99%) percentage value. The surface treatments with mechanical and chemical treatment were done as prescribed by [9, 10].

The prepared mild steel surface was activated in 0.5 M H_2SO_4 for 5 s and immediately rinsed in deionized water.

Table 1 Chemical composition of the mild steel used in the study

Element	% Content	Element	% Content	Element	% Content
C	0.328	Mo	0.096	Ti	0.035
Si	0.973	Ni	0.031	V	0.009
Mn	0.431	Cu	0.113	W	0.006
P	<0.003	Al	0.033	B	<0.002
S	>0.256	Co	0.032	Sn	0.0014
Cr	0.103	Nb	0.014	Fe	99.80

The bath was developed with essential ingredient with $ZnSO_4{\cdot}7H_2O$ 120 g/L, K_2SO_4 20 g/L, Nb_2O_5 nanoparticles 10–20 g/L, $NaSO_4$ 30 g/L, glycine 10 g/L, cetylpyridinium chloride 0.2 g/L, and thiourea 10 g/L. All solute solution was Analar-grade chemicals and was dissolved and prepared by deionized water at room temperature before plating. The prepared bath formulations were allowed to stay for 48 h to obtain suitable homogeneous solution and stirred continuously at 200 rpm with constant heating at 40 °C throughout the plating process. The pH of the prepared solution is observed at 4.8 to achieve good deposition. The choice of the deposition parameter is in par with the study by [12].

The prepared electrode (zinc anode and mild steel which is the cathode) was connected through conductive wire into the rectifier terminals at varying currents between 1.0 and 1.5 A for 20 min. In post-deposition, the coated samples were rinsed in water and air-dried. The produced fabricated coating was sectioned and prepared for characterization. Tables 1 and 2 show the chemical composition analysis of mild steel and formulation-designed bath parameter for the Zn–Nb_2O_5 coatings, respectively.

2.2 Characterization of Coating

The structural characterization of the obtained coatings was evaluated with a VEGA-TESCAN field emission scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). The microhardness properties of the coating were determined by diamond pyramid

Table 2 Electrodeposition parameters and results for the coated mild steel

Sample	Time (min)	C. density (A/dm^2)
Zn–10Nb_2O_5-1.0 A	20	1.0
Zn–10Nb_2O_5-1.5 A	20	1.5
Zn–20Nb_2O_5-1.0 A	20	1.0
Zn–20Nb_2O_5-1.5 A	20	1.5

indenter EMCO Test Dura-scan with a load of 10 g for a period of 20 s. The microhardness values were taken at five difference points on the plated surface with an average means thereafter evaluated on same interval distance.

2.3 Wear and Corrosion Study

The wear schematic diagram for the evaluation of wear mass loss characteristics for this study is presented in Fig. 1, using a CERT UMT-2 tribo-tester at an ambient temperature of 25 °C. The reciprocating sliding tests were done with a load of 5 N, a constant speed of 5 mm/s and displacement amplitude of 2 mm for 20 min with a counter body of Si_3N ball, i.e., 4 mm in diameter, HV 50 g-1600 against all samples. All the samples subjected to wear performance were sectioned into 2 cm by 1.5 cm for perfect hook up by the sample holder.

Sections of the developed sample were subjected to electrochemical corrosion test using Autolab PGSTAT 101 Metrohm potentiostat–galvanostat with a conventional three electrode cell consisting of Ag/AgCl reference, counter and working electrodes. In the electrolytic cell containing 50 mL of 3.65% NaCl solution, the plated sample works as working sample, platinum which works as counter electrode and Ag/AgCl as reference electrode were used. The potentiodynamic potential scan was fixed from −1.5 V to +1.5 mV with scan rate of 0.012 V/s as described by [16]. The following below equation is noted.

$$I_{\text{corr}} = 1/R_p \{(\beta a \beta c)/2.303(\beta a + \beta c)\} \quad (1)$$

Modifying Eq. (1) with Faraday law,

$$\text{CR} = i_{\text{corr}} K \cdot \text{EW}/d \quad (2)$$

where i_{corr} the corrosion current density in A/m^2; K is a constant that defines the units for the corrosion rate; EW is the equivalent weight in grams/equivalent; d is density in g/cm^3; and βa and βc is Tafel slopes of the anodic and cathodic reactions, respectively.

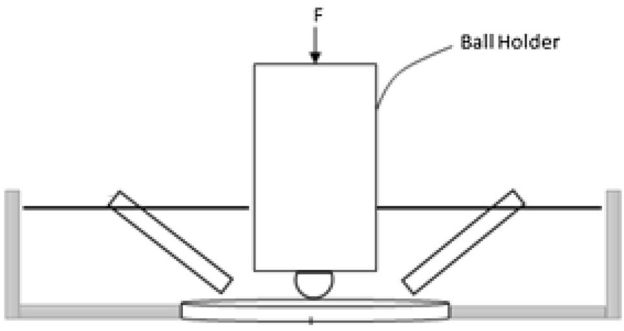

Fig. 1 Schematic view of reciprocating sliding friction CERT UMT-2 test system

3 Results and Discussion

3.1 Morphological Studies

Figure 2a, b, shows the morphological structure of the as-received and Zn–Nb_2O_5 composite coatings at 20 wt% in 1.5 A/dm^2. From Fig. 2a, the steel structure showed a smooth undistorted surface after surface treatment, and this is par with study by [13]. From Fig. 2b, crystallite nodules growth as deposits was seen and distributed on the steel interface. This is clearly showing a perfect incorporation of Nb_2O_5 within the zinc rich. It is important to mention that there are two distinctive phases observed within the interface, one with homogeneous patches at the background and the other like solid flakes in nodular form. However, the microstructural bond was enhanced as anticipated since the nucleation process was instigated from the zinc metal as

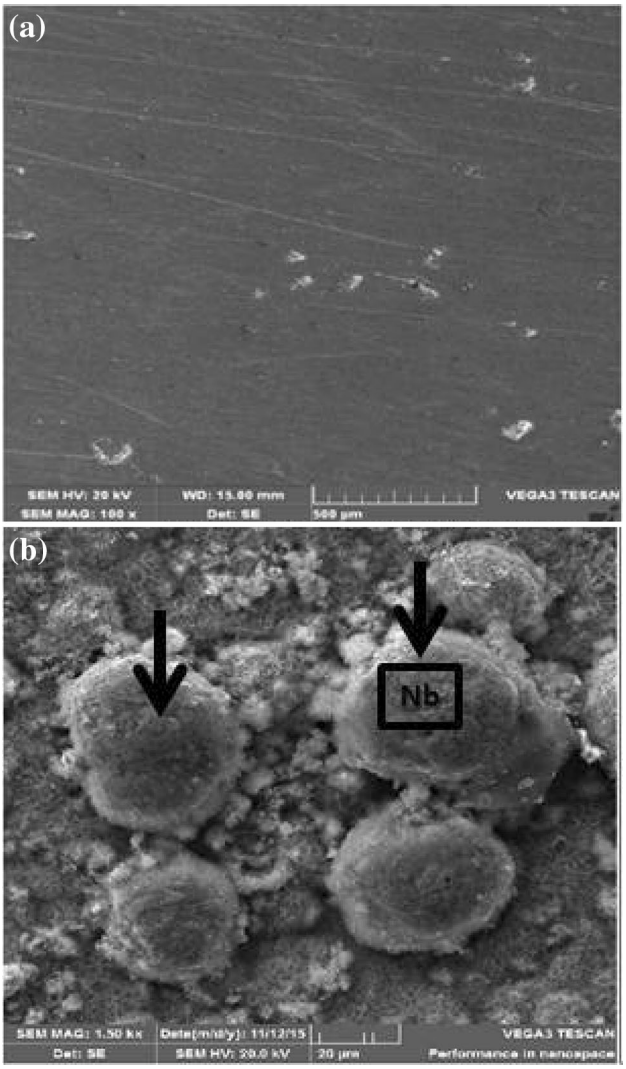

Fig. 2 SEM spectra of **a** as-received mild steel **b** Zn–Nb_2O_5-20 g at 1.5 A/dm^2

load bearing carrier, and the dispersal of the particulate fortified the nucleation spot and strengthened the produced coating. This assertion was supported by [9]. More so, it can also be seen that structural changes are influenced by the applied current densities and the particulate loading effects. At 20 wt% particle loading of Nb_2O_5 zinc, bath produced better precipitation and enhanced surface orientation. Figure 3 shows the EDS pattern of deposited Zn–Nb_2O_5-20 g at 1.5 A/dm^2. The pattern shows combine elemental composition of the fabricated composite coating with indication of Zn, Nb, O present as major element.

3.2 Coating Thickness, Microhardness and Thermochemical Evaluation

The effect of process parameter especially the current densities and particle concentration in wt% was observed on the coating thickness progression in relation to the performance of the coating (see Fig. 4). An increase and decrease in coating thickness were noticed as applied current densities changes. At 1.5 A/dm^2, the fabricated coatings regardless of the particle percentage concentration had a significant higher coating thickness than deposited alloy at 1.0 A/dm^2. However, [3, 8] said that the character of a coating especially in terms of coating thickness against the performance depends on several factors and not necessary a single factor. One could have thought that coating deposited at higher particle concentration will give a better coating thickness trend in all cases which is against assumed expectation. However, Zn–Nb_2O_5-20 g at 1.5 A/dm^2 exhibited higher coating thickness with 196.3 µm and show better performance in all performance consideration than coating produced from Zn–Nb_2O_5-20 g at 1.0 A/dm^2 183.5.

From Fig. 5, a distinctive effect of progression of coating as against the as-received sample was display in a bar-chart profile. All the produced nanocomposite coatings display excellent and unique improvement compared to the

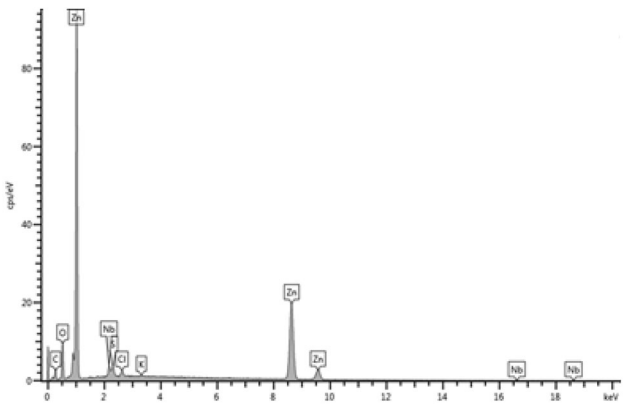

Fig. 3 EDS pattern of fabricated Zn–Nb_2O_5-20 g at 1.5 A/dm^2

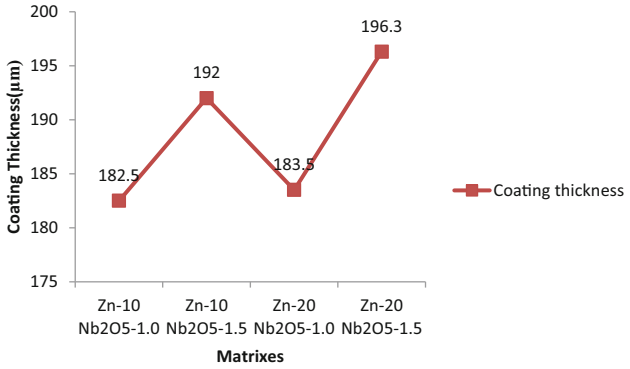

Fig. 4 Coating thickness progression of fabricated Zn–Nb_2O_5 on mild steel

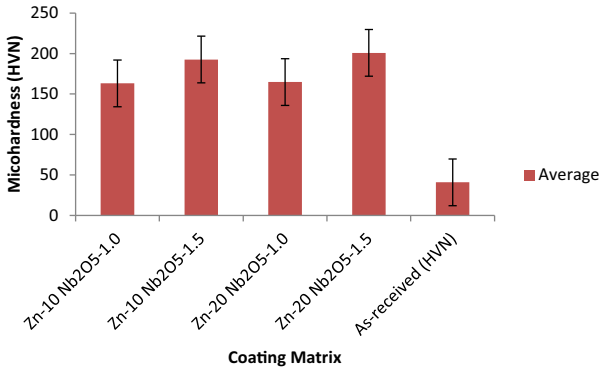

Fig. 5 Microhardness progression of fabricated Zn–Nb_2O_5 on mild steel before heat treatment

control mild steel substrate. Taking cognizance of the trend of coatings from their depth, coating deposited at 1.5 A/dm^2 demonstrated better hardness capacities which can be linked to the robust upshot of the Nb_2O_5 nanosized particulate in the zinc rich. It is good to mention that the sample Zn–Nb_2O_5-20 g at 1.5 A/dm^2 showed the highest hardness property of 200.8 HV compare to the Zn–Nb_2O_5-20 g deposited at 1.0 A/dm^2 with 164.8 HV.

The remarkable improvement of this matrix is principally as a result of strengthening effect which leads to microstructural evolution from the increased quantity of Nb_2O_5 loading into the Zn lattice. Invariably one can say that the microhardness decreased as the supplied current decreased. This change in hardness observed could be assumed to follow the assertion of [15, 16] that coating produced follows some anomaly such as the operating conditions, electrolyte composition and mechanism of diffusion which Faraday's first law of electrolysis governs.

Figure 6 shows the mechanical reaction of the composite coating to heat treatment at 600 °C for 4 h. A general overview shows that the thermal effect could not increase the stability of the coating and in the same vein had solid impact on the degradation tendency. However, a

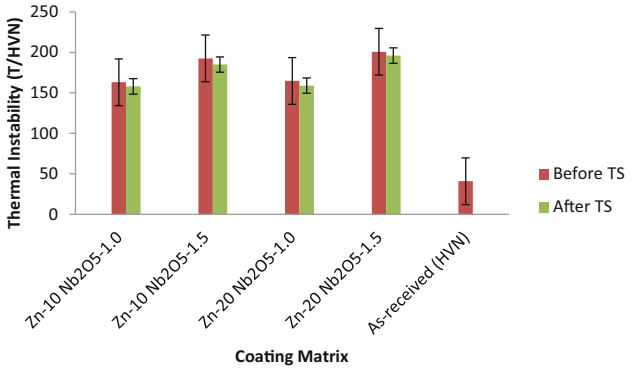

Fig. 6 Thermal stability of fabricated Zn–Nb_2O_5 on mild steel

responsible factor could have been that a solid stable grain refinement occurs but could not project depreciation as a result of solid bond between the deposits and the mild steel substrate. Another careful looks show that thermal treatment enables crystallization growth. However, [16] mention that when annealing takes place beyond the temperature of the based metal often than none, there are possibilities of pill-ups on coating surface. Invariably, the presence of Nb_2O_5 on the zinc rich has been seen to adequately enforce significant stability with less porosity and flaw that might have occurs. Generally, all thermal stability results follow the same trend as that of microhardness trend. The highest thermal stability hardness value is 196 HV/°C for Zn–Nb_2O_5-20 g at 1.5 A/dm^2 with 4 HV deductions to the initial coating of 200 HV.

3.3 Wear Analysis of the Composite Coating on Mild Steel

Figure 7 shows the trend of wear mass loss of Zn–Nb_2O_5 coating at different matrixes on mild steel. The wear mass losses of the fabricated coatings were obviously lesser than that of the control (as-received sample) which is an indication of expected wear resistance properties. One essential observation noticed is that wear loss decreases with increases in the current density and particle loading until 20 g of Nb_2O_5.

In other words, the wear resistance mechanism is influenced by strengthening effect of the embedded admix metal composite in the rich bath. Zn–Nb_2O_5-20 g at 1.5 A/dm^2 had the least plastic deformation tendency of 0.29 g/min compare to 0.92 g/min of the as-received sample. These results imply that the wear resistance was improved by the addition of Nb_2O_5 particles which is par with assertion of [3, 4] that the particulate infringement plays important role in the tribological improvement of most develop alloy as a result of metal matrix composite affinity. Thus, the noticeable wear resistance characteristics revealed the fact that there are less porous, little or no stress initiation and low heterogeneous agglomeration on the outer coating interface which may rather alter the network of coating layer inappropriately during plastic deformation.

3.4 Corrosion Characteristics

The results of the corrosion progression from the linear potentiodynamic polarization study are presented in Fig. 8. In Table 3, the Tafel data were extrapolated to obtain E_{corr}, i_{corr}, corrosion rate (CR) and polarization resistance (R_P), respectively. From the polarization curves of the Zn–Nb_2O_5 composite coating matrices on mild steel, a signification polarization potential E_{corr} value was attained. These characteristics indicate that an increase in additive concentration boosts the progression of corrosion resistance. The developed coatings have resistance to corrosion initiation with lower corrosion rate in series of 6.69E−08 for Zn–20Nb_2O_5-1.5 A mm/year, 3.60E−07 for Zn–10Nb_2O_5-1.5 A mm/year, 4.66E−07 for Zn–20Nb_2O_5-1.0 A mm/year, 4.37E−05 for Zn–10Nb_2O_5-1.0 A mm/year and 2.96E−01 for as-received samples.

Meanwhile, the minimal value for the coating samples with the least corrosion rate shows a good corrosion

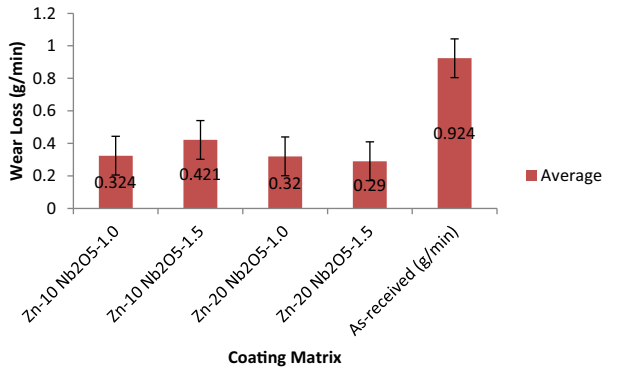

Fig. 7 Wear plastic deformation trend of fabricated Zn–Nb_2O_5 on mild steel

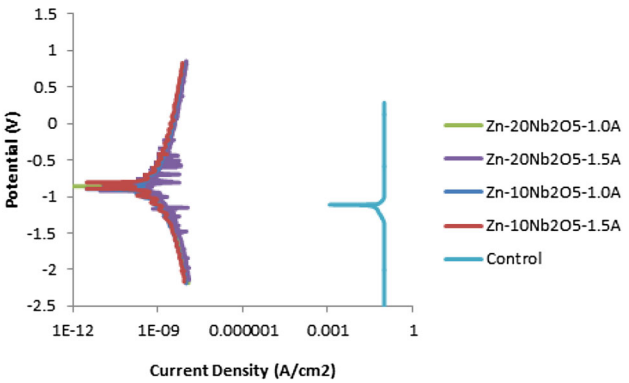

Fig. 8 Potentiodynamic polarization curves of Zn–Nb_2O_5 composite coating on mild steel in 3.65% NaCl solution

Table 3 Polarization data extrapolated from Tafel slope for matrix Zn–Nb_2O_5 composite coating

Sample in 3.65% NaCl	E_{corr} (V)	i_{corr} (A/cm^2)	Corrosion rate (mm/year)	Polarization resistance (Ω)
Control	−1.1500	1.39E−01	2.96E−01	17.05
Zn–10Nb_2O_5-1.0A	−0.99514	1.94E−08	4.37E−05	4.79E+02
Zn–10Nb_2O_5-1.5A	−0.89157	1.81E−08	3.60E−07	4.39E+08
Zn–20Nb_2O_5-1.0A	−0.90103	1.86E−08	4.66E−07	3.62E+08
Zn–20Nb_2O_5-1.5A	−0.86029	1.73E−08	6.69E−08	5.30E+08

potential, which suggests that the incorporation of Nb_2O_5 provides a better corrosion resistance effect. According to [7, 8], this could be credited to the characteristics of the inclusive additive and doggedness of the passive film produced by Zn–Nb_2O_5 coating on the mild steel. Table 3 shows a progressive tabulation of the polarization measurement results, which we obtained from Tafel plots.

4 Conclusion

1. Zn–Nb_2O_5 metal composite coating was successfully fabricated using electrolytic co-deposition route.
2. The structural properties indicate the presence of strong bond Zn–Nb_2O_5 metal composite with EDX pointing to vital elemental constituent.
3. The integration of the Nb_2O_5 nanocomposite particles in the zinc bath as reinforcement improves the tribological and hardness properties of the substrate. The wear plastic resistance and hardness properties increase with increases in the additive concentration.
4. An excellent corrosion resistance of the coating was attained for all deposited coatings as against the as-received samples.
5. The significant performance improvement in the corrosion resistance is as a result of physical barriers produced by Nb_2O_5 nanocomposite particles by filling crevices and lattice exposed by zinc.

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