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Development of Corrosion Resistant Zn-Ni-TiO_2 Composite Coatings

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Abstract- The Zn-Ni-TiO_2 composite coatings were developed on mild steel by electrodeposition method. The bath constituents ($ZnSO_4.6H_2O$, $NiSO_4.6H_2O$, TiO_2, thiamine hydrochloride) and operating conditions (temperature and pH) were optimized by Hull cell method, for peak performance of the coating against corrosion. The coatings were prepared by galvanostatic method at room temperature. The effect of current density (CD), on coating parameters, such as corrosion resistance, thickness and throwing power were studied. The micro hardness of the composite coating was investigated. Potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) methods were used to assess the corrosion resistance of Zn-Ni-TiO_2 composite coatings at different current densities. Surface morphology and composition of the composite coatings was investigated using Scanning Electron Microscopy coupled with energy dispersive spectroscopy (SEM/EDS). Atomic force microscopy (AFM) analysed the topographical surface of the coatings. A new and economical sulphate bath, for bright Zn-Ni-TiO_2 composite coating on mild steel has been proposed, and results are discussed.

Keywords- Composite coating; Mild steel; Current density; Surface morphology; AFM; Throwing power; Hardness

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1. INTRODUCTION

Pure zinc coatings are still commonly used to protect steel from corrosion; significant attempts are being produced to enhance its corrosion resistance for use in harsher environments [1]. Due to its good corrosion resistance, steel is currently widely used in multiple applications. However, steel is susceptible to corrosion in warm dilute sulfuric acid in certain sectors, such as the synthetic fiber sector, waste heat recovery, and alternative energies (i.e., proton exchange membrane (PEM) fuel cells and water electrolysis hydrogen manufacturing). Because steel passivation is not stable, corrosion strength reduces in acidic media .[2]

Composite materials have multiple characteristics such as hardness, resistance to high temperature oxidation, great wear and resistance to corrosion. The new composite materials are synthesized by various current techniques because of their significance in many areas. Among these methods, electrodeposition is regarded one of the most significant composite production techniques due to accurately monitored operation to room temperature, fast deposition rates, and low cost. Several literatures appear in science publications linked to SiC, ZrO_2, Al_2O_3, and TiO_2 with single metal and alloy electrodeposition [3-5]. Zn-Ni-TiO_2 composite coatings from a commercial electrolyte comprising suspended TiO_2 nanoparticles were electrodeposited on mild steel. XRD and SEM-EDAX techniques researched the structure, morphology and chemical structure of the Zn-Ni coatings, and electrochemical measurements assessed the corrosion resistance. The impact of TiO2 nanoparticles on structure, morphology and corrosion characteristics in the deposition bath is discussed [6]. According to Brenner [7], anomalous electrodeposition of Zn-Ni alloys happens (reduction of less noble zinc is preferential), either owing to hydroxide suppression mechanism (release of more noble ions is impeded by the formation of $Zn(OH)_2$ to normal pH increase). In latest years, Zn-Ni alloys have drawn considerable attention due to their greater corrosion resistance and better mechanical properties than pure Zn and other alloy coatings for steel parts based on Zn [8]. For industrial applications, however, demand for Zn-Ni coatings with better mechanical and corrosion characteristics is growing. Ramesh Bhat et. al. [9, 10] studied the fabrication of Zn-Ni, and optimization Zn-Co alloy coatings on mild steel from acid chloride and acidic sulphate bath and its corrosion performance. Recently Zn-Ni composite coatings have been developed to meet industry requirements to improve mechanical and chemical properties [6].

In the present work, attempts were produced to use an electrolytic technique to create Zn-Ni-TiO_2 composite coatings on mild steel. Corrosion resistances, microstructure of the deposit and mechanical properties such as hardness, thickness and throwing power have been researched.

2. EXPERIMENTAL METHOD

Mild steel plates were purchased from High-tech sales corporation, Mangalore. The basic compositions of mild steel are 0.063-C, 0.23-Mn, 0.03-S0.011-P and balance-Fe. The mild steel (MS) specimen was taken in the form of a 4cm×2.5cm exposed surface areas, remaining was entrenched in epoxy resin. According to metallographic practice, the specimen was subjected to belt grinding, polishing using different grades of emery and velvet mop wheels to obtain mirror finish. Then the specimen was cleaned with double distilled water followed by trichloroethylene, finally dried and immediately used as cathode for the analysis.

Analytical grade chemicals and distilled water were used to prepare the electrolytic bath solutions. The bath compositions were optimized using Hull cell technique. All coatings at 30°C and pH=4.0 were performed, except during their deviation. Plating baths were adjusted to pH 4.0 with dilute solutions of H_2SO_4 and Na_2CO_3 whenever necessary. The cleaned MS substrate had exposed area of 10 cm^2 was used as a cathode and same area of pure Zn plate as anode. A 250 ml rectangular glass electrolytic cell with a cathode anode distance of ~5cm has been used. All depositions were galvanostatically performed under the same temperature and pH circumstances for 10 minutes (for assessment) using very sophisticated DC power analyzer (N6705C, Keysight Technologies India Pvt. Ltd). THC has been used as complexing agent for the deposition. Based on the surface morphology of the deposit, bath compositions and deposit conditions were optimized.

Potentiostat (CH604 E-series, U.S. model with CH instrument beta software) was used to perform electrochemical test results in 3.5% NaCl solution. The standard arrangement of three-electrode cells was used. The working electrode (WE) was a coated MS with 1 cm^2 exposed surface area. The counter electrode was a platinum foil. The reference electrode was a saturated calomel electrode (SCE). The corrosion activities of the deposit were studied by PP method and EIS method. PP measurements were done by polarizing the specimen from −200mV cathodically to +200mV anodically with respect to open circuit potential (OCP) with a scan rate of $1mVs^{-1}$ and the potentiodynamic current - potential plots were recorded. Corrosion data such as corrosion potential (E_{corr}), anodic and cathodic Tafel slope are βa, βc, corrosion current density (i_{corr}) were obtained from the software installed in the CH instrument. The EIS measurements were made over a frequency range of 100 kHz to 10 mHz at AC potential of ±10 mV.

Haring–Blum cell was used to determine the throwing power (TP) of the plating bath and is given by the equation [9]:

$$Throwing\ power\ (\%) = \frac{X - Y}{X + Y - 2} \times 100 \tag{1}$$

where X is the distance ratio from the anode of far and near cathodes, and Y is the mass ratio of deposits on near and far cathodes.

Vickers technique used Micro Hardness Tester (CLEMEX) to determine the hardness of the coating film (~20 µm) at a load force of 50 g for 20 sec at room temperature. For each sample, 10 measurements were taken. The thicknesses of the coatings were determined from Faraday's equation:

$$t = \frac{(E \times Ic \times CE \times \Delta t)}{d \times F} \tag{2}$$

where t is deposit thickness, E is equivalent weight, I_C is deposit current density, CE is current efficiency, Δt is time period, and d is density of coating and F is Faradays constant (96,500 Coulombs). The measured thickness was confirmed by using a digital thickness meter.

Surface morphology of Zn-Ni-TiO_2 coating at different current density was carried out by using analytical scanning electron microscope (JEOL JSM-6380L), in the magnification of 1000X and Atomic Force Microscope (AFM, Nanosurf Flex AFM, and Switzerland). The composition of the Ni and Ti were analyzed by EDS. The reflectivity of the deposit was measured using gloss meter (Nova-Elite, 60^0, ASTM D2457).

3. RESULTS AND DISCUSSION

3.1. Optimization of bath

Acid sulfate bath with $ZnSO_4.7H_2O$, $NiSO_4.7H_2O$, $C_6H_8O_7.H_2O$, $CH_3COONa.3H_2O$, $C_{12}H_{17}N_4OSCl.HCl$ and TiO_2 has been optimized using regular Hull cell technique [11]. The addition of small quantities of thiamine hydrochloride (THC) has been found to have a significant impact on the deposit brightness. As a buffer, citric acid (CA) was used to prevent the formation of hydroxide. TiO_2 has been used as a composite material for deposit. Wide range of CD, 1.0-7.0A/dm^2 was acquired for deposits with a white/grayish white / bright / porous bright appearance. Sodium acetate has been used as a conducting salt to improve the homogeneity of the deposit.

Table 1 The bath components and working parameters of optimized bath for Zn-Ni-TiO_2 composite coating on mild steel at 303K

Bath composition	Amount in g/L	Operating parameters
$ZnSO_4.7H_2O$	100	pH: 4.0 Temperature: 303 K Anode: Pure zinc Current density: 5.0 A/dm^2
$NiSO_4.7H_2O$	80	
$CH_3COONa.3H_2O$	60	
$C_{12}H_{17}N_4OSCl.HCl$	0.6	
$C_6H_8O_7.H_2O$	3.0	
TiO_2	3.0	

The effect of each component on the appearance, brightness and morphology of the coatings was examined in terms of their impact. Table 1 shows the bath components and working parameters after optimization.

3.2. Effect of Current density

Using optimized baths, wt% Ni and Wt%TiO_2 is determined with the effect of CD's [12]. It was revealed that CD plays a significant role in both coating appearance and corrosion performance of the deposit. Change in the appearance of the composite coating depending on the composition of Ni and TiO_2 over a broad spectrum of 1.0-7.0 A/dm^2 is given in Table 2. The bath produced grayish white deposit at low c.d. side and produces a porous bright deposit at high c.d. A smooth deposit was found at 5.0 A/dm^2 with ~44wt.% Ni and 1.78 wt% Ti analyzed by EDS. Increase in Ni content with current density is attributed to the rapid depletion of more readily depositable Zn^{2+} ions at the cathode coating [3].

Table. 2 Effect of current density (CD) on TP, hardness, Thickness, glossiness and nature of Zn-Ni-TiO_2 coatings from optimized bath

CD's (A/dm^2)	TP (%)	VHN	Thickness (µm)	Glossiness	Appearance of deposit
1.0	16	142	7.3	136	White
2.0	21	158	12.7	159	Grayish white
3.0	31	168	15.6	187	Semi Bright
4.0	39	170	17.5	203	Bright
5.0	45	185	19.8	254	Bright
6.0	34	183	21.7	261	Porous bright
7.0	29	180	25.4	221	Burnt porous

3.2.1. Hardness, Thickness, Glossiness, Tthrowing power and CCE of deposit

Hardness, thickness, glossiness and throwing power of the Zn-Ni-TiO_2 composite coating was found to increase with CD as shown in Table 2. The Vickers micro hardness values obtained from different current densities of Zn-Ni-TiO_2 electrodeposited on mild steel are shown in Fig. 1. The development of coating micro hardness showed increases with increase in CD's. This may be ascribed by the high density of Ni, compared to Zn and Ti (d_{Zn}= 7.14 g/cm^3, d_{Ni} = 8.90 g/cm^3 and d_{Ti} = 4.506 g/cm^3). But at high c.d. the coating was thick and hard. However, at very high c.d., due to the deposition of metal hydroxide caused by excessive evolution of hydrogen during plating, the deposit was dense and flaccid.

The functional CD was found to show direct dependency on thickness of deposit as given in Table 2. The observed linear dependency of deposit thickness with increase in CD may be due to the adsorbed metal hydroxide at the cathode, caused by the steady increase of pH due to evolution of hydrogen gas at the cathode.

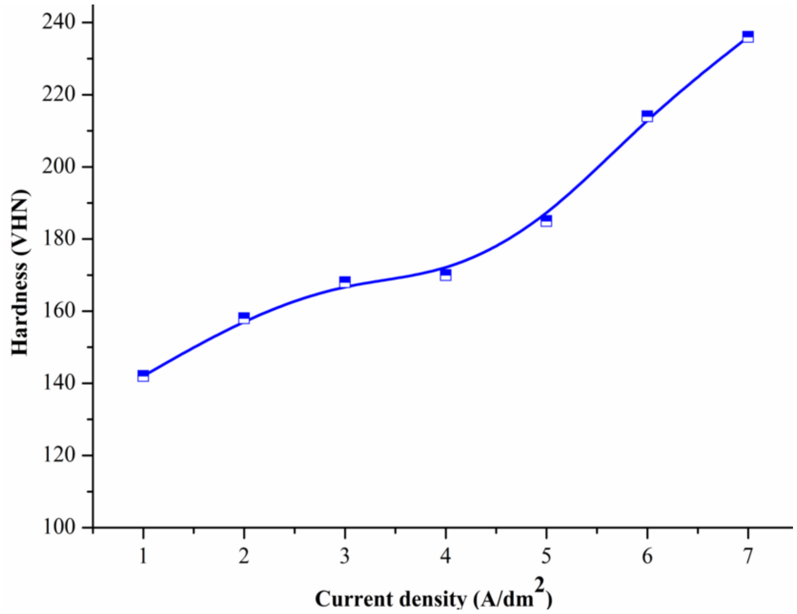


Fig. 1. Vickers microhardness of Zn–Ni-TiO_2 composite coatings from optimal bath at different current densities

The glossiness of Zn-Ni-TiO_2 composite coatings at different CD's was also tested and it was found that the deposit formed at low CD showed least glossiness, whereas at the optimum CD, the glossiness was found maximum. At higher CD, glossiness decreased due to increased porosity.

Throwing power of optimized bath at low CD, 1A/ dm^2 was found to be very small 16%. Throwing power was found to be good at 5A/dm^2 (45%). Further increase in CD above 5 A/ dm^2, reduces throwing power to 29% at 7A/ dm^2.

3.3. Corrosion Study

3.3.1. Tafel Method

Potentiodynamic polarization performances of Zn-Ni-TiO_2 composite coatings, plated at various CD's are shown in Fig. 2. Corrosion characteristics including corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were obtained by Tafel extrapolation method from the PP curves, and are summarized in Table 3. From experimental data it can be pointed out, the coating deposited at 5.0 A/dm^2, having 44.18 wt. %of Nickel and 1.78 wt% of TiO_2 demonstrates excellent resistance to corrosion with a minimum i_{corr} =6.421µA/dm^2. This is further supported by its dense surface morphology (Fig. 3b). Further increase in Ni content, however, led to an increase in corrosion rate, i.e. due to its thick porous structure, the highest i_{corr} values of were seen at higher current density (Table 3 and Fig. 3c).

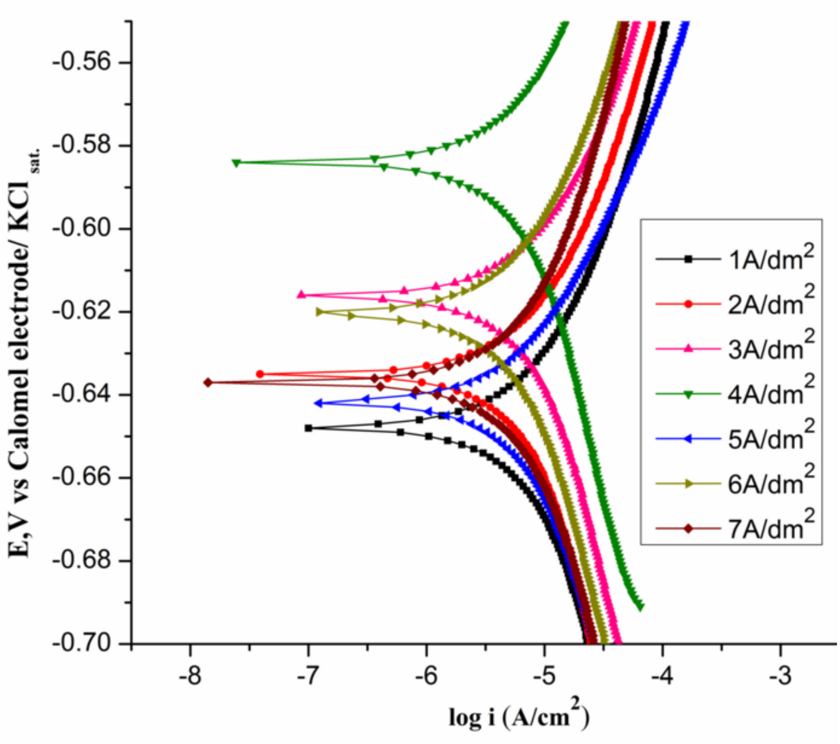


Fig. 2. Potentiodynamic polarization plot of Zn-Ni-TiO_2 alloy coatings developed from optimized bath at different current densities

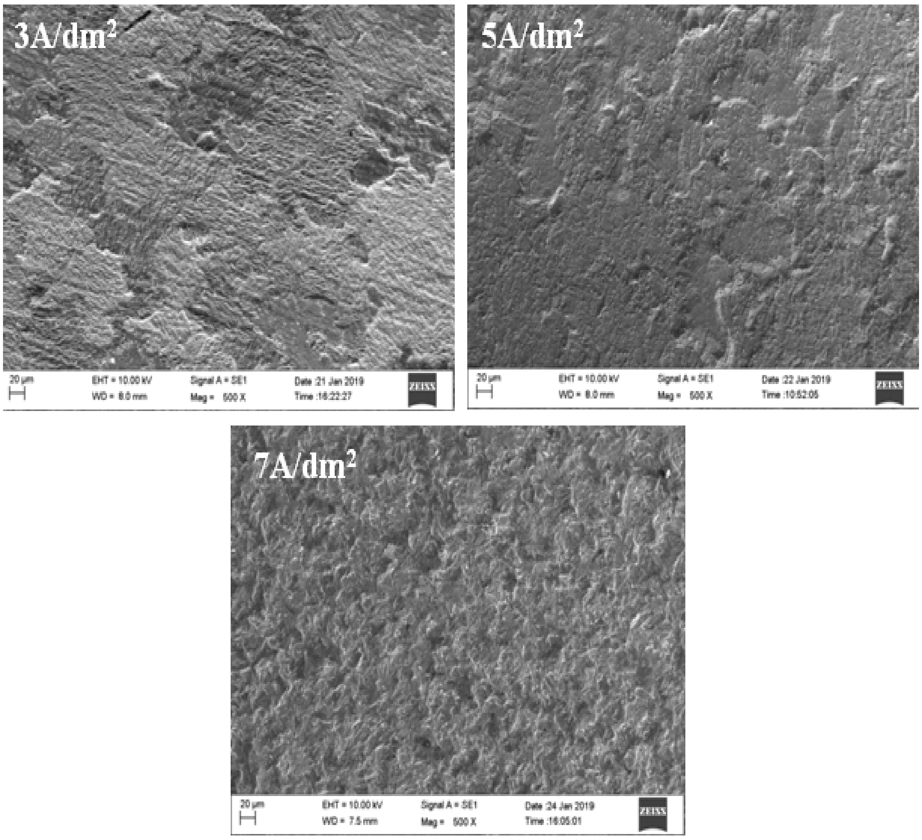


Fig. 3. SEM micrographs of Zn-Ni-TiO_2 coatings formed at different current densities from the optimized bath: a) 3A /dm^2 b) 5A/dm^2 and c) 7A/dm^2

Table 3. Polarization results for Zn-Ni-TiO_2 coatings in 3.5 % NaCl solution from various current densities from optimal bath

C.D (A/dm^2)	-E_{corr} (V)	βc	βa	i_{corr} (μA/dm^2)
1	0.6480	9.98	14.54	10.881
2	0.6350	7.72	12.62	8.741
3	0.6160	9.76	15.52	7.756
4	0.5840	9.25	12.39	7.105
5	0.6420	11.13	17.11	6.421
6	0.6200	10.18	14.18	9.767
7	0.6370	12.20	18.97	11.162

3.3.2. EIS Studies

The EIS is a useful technique to rate coatings, determine interfacial reactions, measure coating breakdown and estimate the lifetime coating / metal systems. The advantages of this technique over *DC* technique include the absence of any major perturbation *of* the system, its applicability to low conductivity media evaluation, and the presence of a frequency portion that can provide mechanistic information.

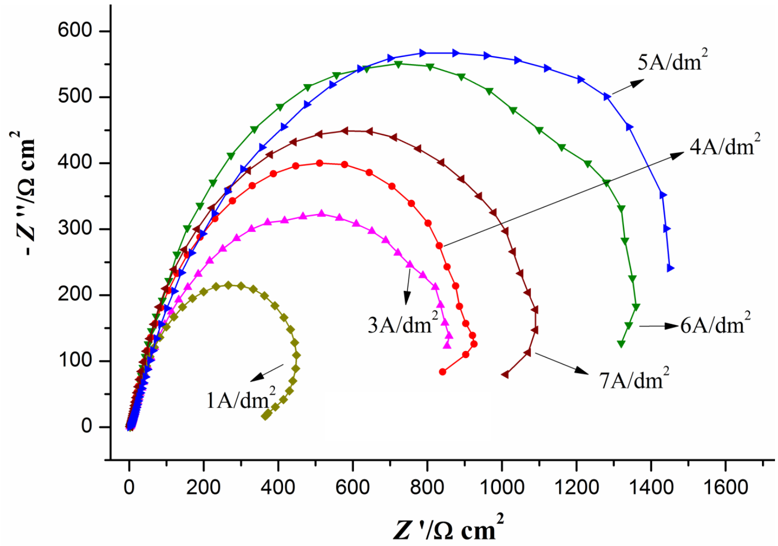
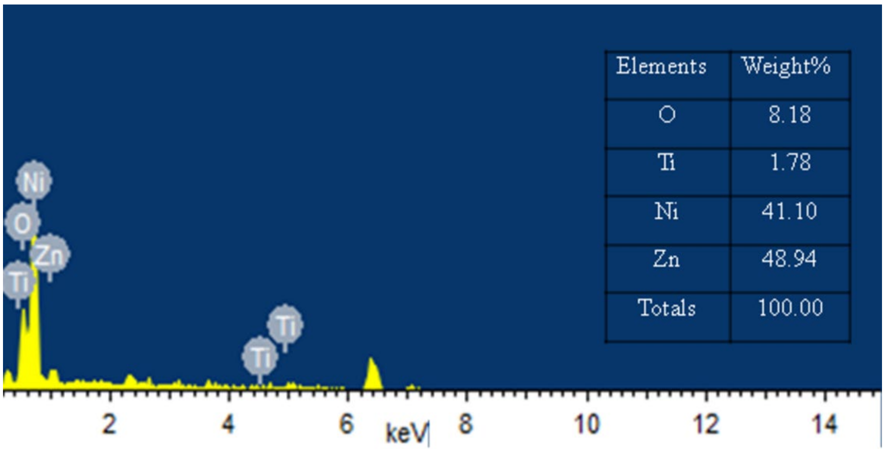


Fig. 4. Nyquist plot for Zn-Ni-TiO_2 coatings at various current densities from optimal bath at different current densities

The efficiency of Zn-Ni-TiO_2 composite coatings in corrosion was evaluated using the EIS method. The most powerful method is the Nyquist plots, which usually plot the data as imaginary impedance (Z_{img}) vs real impedance (Z_{real}) with the provision to distinguish the contribution of polarization resistance (Rp) vs solution resistance (Rs). The EIS responses of Zn-Ni-TiO_2 coatings, obtained at different CD's, are shown in Fig. 4. The EIS responses of all coatings display only one depressive loop across the entire frequency spectrum. This indicated the capacitance of the electrochemical system under research, electrical double layer (EDL) is responsible for improving the corrosion safety of the deposit. The bigger diameter of the semicircle in case of coatings at 5.0 A/dm^2 reflects larger corrosion resistance, which is attributed to a change in the coating capacitance.

3.4. SEM study

The changes in the surface structure of the deposits can be observed from the SEM analysis. Fig. 4 shows the surface topography of Zn-Ni-TiO_2 coating at different CD's. It was observed that at low CD (3A/dm^2) the deposit is thin and grayish white with dull appearance (Fig. 3a). Relatively smooth, uniform and bright deposit was obtained at optimal CD = 5.0 A/dm^2 (Fig. 3b) and at higher CD=7.0 A/dm^2, porous and rough deposit due to high content of Ni and TiO_2 was shown in Fig.4c. The wt. % Ni and wt.%TiO_2 at optimum CD=5A/dm^2 was determined by EDS analysis (Fig. 5) and the corresponding wt.%Ni and wt.%TiO_2 content in the deposits are 44.1% and 1.78%.



Elements	Weight%
O	8.18
Ti	1.78
Ni	41.10
Zn	48.94
Totals	100.00

Fig. 5. EDS plot of Zn-Ni-TiO_2 composite coating at the optimal CD., i = 5.0 A /dm^2

3.5. AFM study

Fig. 6a-c displays the 2D and 3D images of Zn-Ni-TiO_2 composite coatings at various current densities, (3A/dm^2, 5A/dm^2 and 7A/dm^2) respectively. The mean roughness Ra was calculated using Atomic Force Microscope (AFM, Nanosurf Flex AFM, and Switzerland) based on AFM images. The roughness values (Ra) of Zn-Ni-TiO_2 composite coatings with various current densities were 28.6, 24.8 and 38.1 nm. Thus, it can be concluded that the Zn-Ni-TiO_2 composite coating were less coarse and textured smooth, homogeneous, compact and exhibited small peaks of normal grain size, resulting in higher corrosion resistance at the optimal CD 5A/dm^2 (Fig. 6b) and has a lower roughness (Ra=24.8 nm) than other current densities.

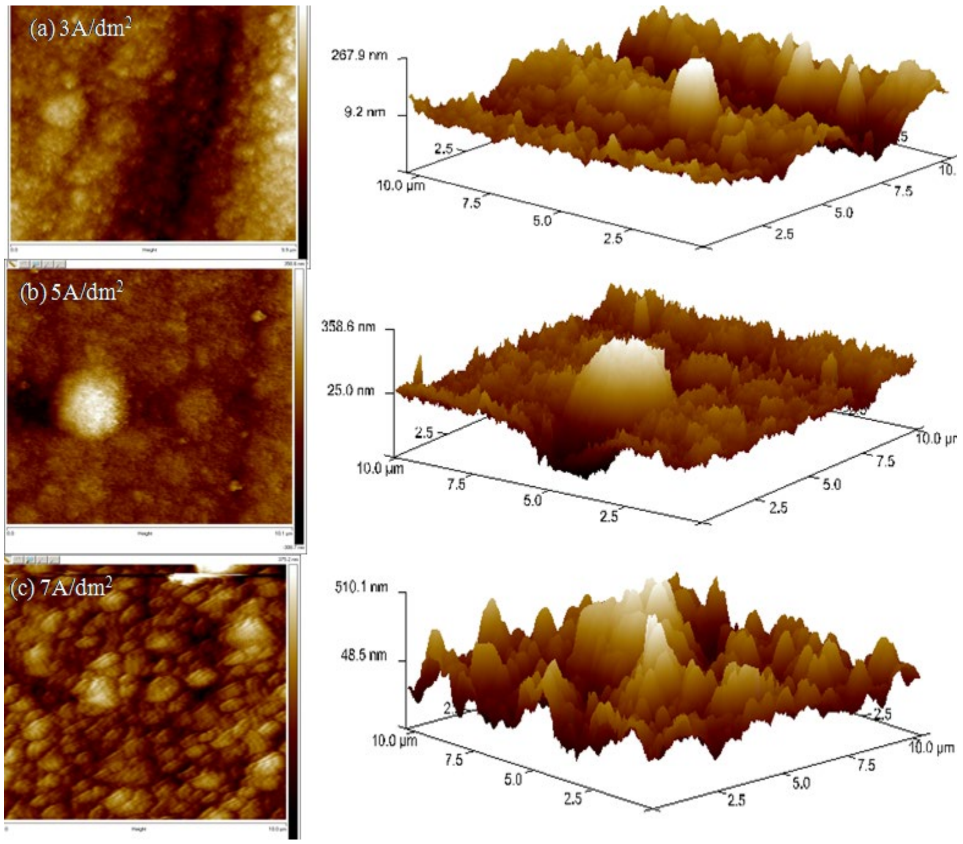


Fig. 6. 2D and 3D images of Zn-Ni-TiO_2 composite coatings at various CD's from the optimized bath: (a) 1A/dm^2, b) 5A/dm2 and c) 7A/dm^2

Fig. 6a, the deposition was uniform with dull appearance and had little higher peaks and roughness (Ra=28.6). Fig.6c, the deposition was non-uniform and had a high peak of larger grains, indicating the highest roughness (Ra=38.1). The additives were preferentially adsorbed into the matrix of Zn-Ni-TiO_2 and inhibited the composite coatings of Zn-Ni-TiO_2, resulting in a smaller reduction of Zn^{2+} and Ni^{2+} on these matrices, and thus smooth and homogeneous deposits were observed [13]. The roughness factor reflects the initial surface irregularities and non-uniformity; thus, an irregular surface shows a higher rate of dissolution, particularly when a corrosive environment is present [14]. This surface factor indicates that the uniformity of the coating deposited from a sulphate bath is not linearly dependent [15, 16].

4. CONCLUSION

The electrochemical behavior of Zn-Ni-TiO_2 composite coatings was developed from acid sulphate bath using standard Hull cell method. Based on the existing findings, it could be inferred that the nickel ions and TiO_2 particles in the plating solution and the present deposition CD had a major effect on the chemical composition, morphology and corrosion stability of Zn-Ni-TiO_2 coatings. Based on EDS, the electrodeposits having about 41.1 wt.% Ni and 1.78 wt.%

of TiO_2 and was found to be very smooth and stable, showing outstanding corrosion resistance and having the lowest i_{corr} value (6.421 μA/dm^2). The deposit's thickness, hardness, and glossiness are directly dependent upon wt. %Ni and wt% of TiO_2 in the composite. The AFM and SEM methods have disclosed the development of composite coating on the mild steel surface in terms of morphology, topography and roughness of the surface at various CD's.

REFERENCES

[1] V.G. Roev, R. A. Kaidrikov, and A. B. Khakimullin, Russ. J. Electrochem. 37 (2001) 756.

[2] A. Gahoi, S. Wagner, A. Bablich, S. Kataria, V. Passi, and M. C. Lemme, Solid-State Electronics 125 (2016) 234.

[3] M. D. Ger and R. Grebe, Mater. Chem. Phys. 87 (2004) 67.

[4] P. A. Gay, P. Bercot and J. Pagetti, Surf Coat Tech.140 (2001) 147.

[5] Y. Yao, S. Yao, L. Zhang and H. Wang, Mater. Lett. 61(2007) 67.

[6] D. Blejan, D. Bogdana, M. Popb, A.V. Popa, and L.M Muresan, Optoelectron. Adv. Mat. 5 (2011) 25.

[7] A. Brenner, Electrodeposition of Alloys, Principles and Practice, Academic Press, New York and London, 77 (1963).

[8] M. M. Abou-Krisha, J. Coat. Tech. Res. 9 (2012) 775.

[9] R. S. Bhat, S. Bekal and A. C. Hegde, Anal. Bioanal. Electrochem. 10 (2018) 1562.

[10] R. S. Bhat and A. C. Hegde, Anal. Bioanal. Electrochem. 6 (2014) 606.

[11] Pardhasaradhy. Practical Electroplating Hand Book, Prentice Hall Incl. Pub., Chapter 3 , (1987).

[12] A. I. Vogel, Quantitative Inorganic Analysis, Longmans Green and Co, London (1951).

[13] M. G. Hosseini, H. Ashassi-Sorkhabi and H. A. Y. Ghiasvand, Surf. Coat. Technol. 202 (2008) 2897.

[14] Y. Lin and J. Selman, J. Electrochem. Soc. 140 (1993) 1299.

[15] Z. Feng, Q. Li, J. Zhang, P. Yang, H. Song and M. An, Surf. Coat. Technol. 270 (2015) 47.

[16] Z. Feng, Q. Li, J. Zhang, P. Yang and M. An, RSC Adv. 5 (2015) 58199.