Journal of Alloys and Compounds 654 (2016) 561–566

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Surface characterization, mechanical properties and corrosion behaviour of ternary based Zn–ZnO–SiO_2composite coating of mild steel

A.P.I. Popoola [a], V.S. Aigbodion [a, b, *], O.S.I. Fayomi [a, c]

[a] Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa
[b] Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Nigeria
[c] Department of Mechanical Engineering, Covenant University, P.M.B 1023, Ota, Ogun State, Nigeria

ARTICLE INFO

Article history:
Received 18 August 2015
Received in revised form
7 September 2015
Accepted 11 September 2015
Available online 14 September 2015

Keywords:
Mechanical improvement
Microstructure
Zn–ZnO–SiO_2 and wear loss

ABSTRACT

Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions. Because of the pollution and high cost associated with cyanide, deposition from other baths is gaining importance. In order to develop a bath with additive that could produce a quality coating is the motivation behind this present work which is surface modification of Zn–8ZnO–SiO_2 nano composite coating on mild steel surface by electrodeposition route. The influence of SiO_2 on Zn–8ZnO sulphate electrolyte on the properties and microstructure of the produced nano-coatings were investigated. The SiO_2 was varied from 0 to 16wt%. The microstructure characteristics of these produced series composites coating were investigated using scanning electron microscopy couple with energy dispersive spectroscopy (SEM/EDS), X-ray diffraction and atomic force microscopy (AFM). The corrosion degradation properties in 3.65% NaCl medium were studied using potentiodynamic polarization technique and characterized by high resolution optical microscope (HR-OPM). The hardness and wear of the composite coating were measured with high diamond microhardness tester and dry abrasive MTR-300 testers respectively. The results showed that average hardness value of 142.5 and 251.2HV and corrosion rate of 0.13088 and 0.00122 mm/yr were obtained for the 0 and 16wt% SiO_2 in Zn–8ZnO. The work have established that upto 16% SiO_2 in Zn–8ZnO composite coating on mild steel can be used in improving the microhardness, wear loss and corrosion resistance of mild steel.

1. Introduction

Zinc coatings are considered as one of the main methods used for the corrosion protection of steel. The usage in industrial sectors as a protective coating for large quantities of products and other fabricated ferrous metal parts are enormous [1–3]. Acid zinc bath are used where it is desirable to have a high plating rate with maximum current efficiency and good deposition depends mainly on the nature of the bath constituents [4,5].

Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions. Because of the pollution and high cost associated with cyanide, deposition from other baths such as sulphate, chloride, and mixed sulphate-chloride baths are gaining importance [6,7]. Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, complexing agents and metal ions. Among these the complexing agents influence the deposition process, solution properties and structure of the deposit. The action of these complexing agents depends on pH, nature of anion, temperature and other ingredients of the medium [8,9].

Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit [10–12]. Therefore, there are lots of R & D works, carried out during the last two decades, regarding to the production of zinc alloy coatings used to replace zinc coating. Tiwari et al. [13] made an attempt to increase the corrosion resistance of mild steel (MS) by depositing alumina coating,. Masao et al. [14] reported on the formation of $TiAl_3$ coating on a TiAl substrate by electro-deposition of Al from the DMSO2 bath and subsequent annealing to demonstrate the

* Corresponding author. Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa.
E-mail addresses: popoolaAPI@tut.ac.za (A.P.I. Popoola), victor.aigbodion@unn.edu.ng (V.S. Aigbodion), ojosundayfayomi3@gmail.com (O.S.I. Fayomi).

http://dx.doi.org/10.1016/j.jallcom.2015.09.090
0925-8388/

feasibility of this process. Pedroza et al. [15] studied the effect of glycerol in Zn–Ni bath content to improve the corrosion resistance of carbon steel substrates in several applications. Dikici et al. [16] investigated the mechanical and structural properties of Zn–Ni–Co ternary alloy electroplating on mild steel and contrasted with the characteristics of Zn–Ni and Zn–Co alloy coatings. Chuen-Chang et al. [17] reported on the electro-deposition of zinc-nickel alloys on steel by pulse current. According to Shivakumara et al. [2] the effective process of surface co-deposition of a metal is electro-deposition with variety of alloying elements. The deposited layer is strongly bonded to the substrate with very fine microstructure in the deposition area due to alloying element additions; current supplied, the voltage, the composition of the cathode substrate, time of immersion and plating baths composition. Also the service life of zinc coating is enhanced by including the inert materials in its coating. The inclusion is done by co-deposition of these materials with zinc and thus generating composite coating [7]. These zinc composite coatings exhibit better corrosion resistance. Nowadays the nanosized materials are co-deposited to get better zinc coating composite with better corrosion resistance [8]. Researches in the area of zinc coatings on steel are rather unending because of the unique properties and the very low cost that it offers. In this study an attempt to develop a compactable and structural modified coating that will work against chemical and mechanical deterioration with the help of Zn–8ZnO–$SiO_2$was studied.

2. Experimental procedure

2.1. Preparation of substrates and fabrication of coating

Flat specimens of commercial mild steel of (30 mm × 20 mm × 1 mm) sheet was used as cathode substrate and zinc sheets of (50 mm × 30 mm × 2 mm) were prepared as anodes. The initial surface preparation was performed with the fine grade of emery paper, properly cleaned with sodium carbonate, descaled/pickled and activated with 10% HCl at ambient temperature for 10 s then followed by instant rinsing in deionized water. The cathode was made of mild steel coupons and the anode used commercially 99.99% pure zinc obtained from SERC research centre, Pretoria, South Africa. The solutions for plating were prepared a day prior to the tests. ZnO (50 nm) and SiO_2 (20 nm) nanoparticles added into the bath were kept in suspension for 18hrs using a magnetic stirrer to prevent agglomeration of particles in the solution. The bath % composition were described in Table 1 and deposited designed are presented in Table 2. The pH of the bath solution was kept constant at 4.5 and adjusted by addition of HCl or NaOH. All the experiments were conducted under ambient conditions and the plating time was 15 min at a magnetic stirring speed of 200 rpm. After electrodeposition, the plated samples were rinsed in water for 5 s and then left to air dry.

Table 1
Bath composition of Zn–ZnO–SiO_2 alloy co-deposition Matrix.

Composition	Mass concentration (g/L)
$ZnSO_4.7H_2O$	100
SiO_2	8–16
ZnO	8
Boric acid	5
Glycine	5
Thiourea	5
Temp	40 °C
pH	4.5
Time	15 min
Current Density	1.0 A/cm^2

Table 2
Formulated designed bath composition of Zn–ZnO–SiO_2.

Sample order	Matrix sample	Time of deposition (min)	Current (A/cm^2)
1	Zn–8ZnO	15	1.0
2	Zn–8ZnO–8SiO_2	15	1.0
3	Zn–8ZnO–12SiO_2	15	1.0
4	Zn–8ZnO–16SiO_2	15	1.0

2.2. Structural studies

Microstructure evolution was characterized on OlympusBX51M Optical Microscope (OM) and Jeol JSM6510 Scanning Electron microscopy (SEM) built with EnergyDispersive Spectroscopy (EDS). X-ray diffraction (XRD) was done using the Rigaku/Dmax 2200 pc automatic X-raydiffractometer with Cu target Ka radiation to identify the phase change.

2.3. Microhardness characterization

Micro-hardness of the deposited coatings was evaluated by using dura diamond indenter microhardness tester within built camera. A load of 10 g was used during the tests with a withholding time of 10 s. The values recorded are an average of 4 measurements obtained from different locations.

2.4. Wear studies

MTR 300 dry abrasion rig machine was used to determine the percentage wear mass loss under dry medium using silica sand as a wearing medium at a speed of 200 rev/min for 60 s. The initial mass of the deposited samples were weighed before the tests and the final masses were recorded after the dry sliding. These values were used to determine the percentage wear mass loss.

2.5. Electrochemical studies

Linear potentiodynamic polarization technique was used to investigate the corrosion resistance of the coatings in 3.65% NaCl solution using μAUTOLAB Pontentiostat/Galvanostat. The polarization measurements were carried from a potential of −1.5–1.5 V with a scanning rate of 0.021 V/s.; saturated calomel electrode was used as a reference and graphite served as a counter electrode. The coated samples were used as working electrode with an exposed area of 1 cm^2. Nova 1.8 was used to extrapolate the corrosion parameters obtained from the Tafel curves.

3. Results and discussion

3.1. Microstructural and XRD studies

Figs. 1–2 showed the scanning electron micrographs and attached EDS of the samples. In general from deposition appearance the whole plating displays better plating and good adhesion. The nature of the surface morphology and orientation in unveiled the homogeneous appearance with good dispatches as expected. One significant reason for this behaviour might be as results of the deposition parameter. In Fig. 2, there was spherical shaped, with clumped distributions are visible through the SEM analysis. From the SEM it is observed that the Zn–8ZnO–16SiO_2 composite coating is roundish while some are angular in shape and longitudinal. The Zn–8ZnO–16SiO_2 surface morphology plays a vital role in case of composite coating materials. External surface features of particles such as contours, defects and damage and surface layer

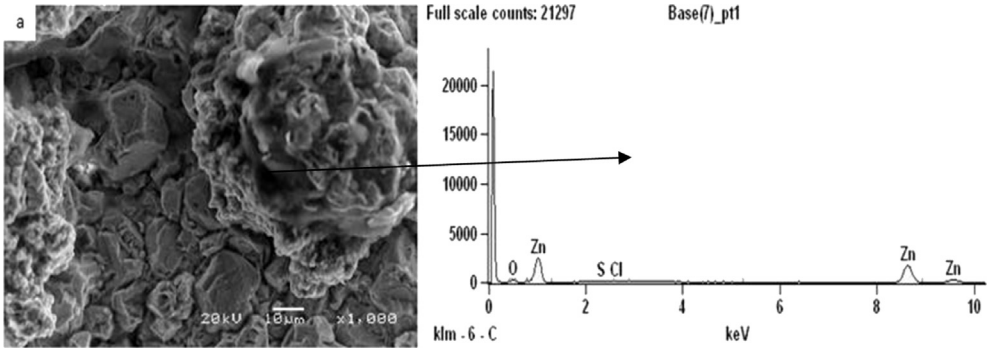

Fig. 1. SEM/EDS morphology of Zn–ZnO deposited at 1 A/cm^2 for 15 min.

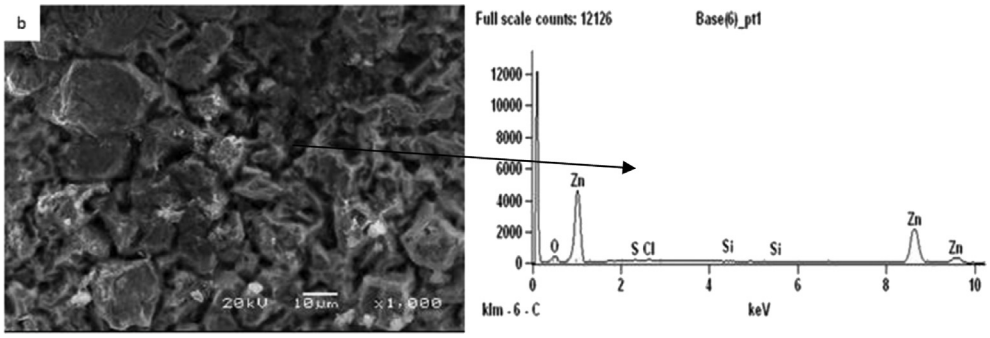

Fig. 2. SEM/EDS morphology of Zn–8ZnO–16SiO_2deposited at 1 A/cm^2 for 15 min.

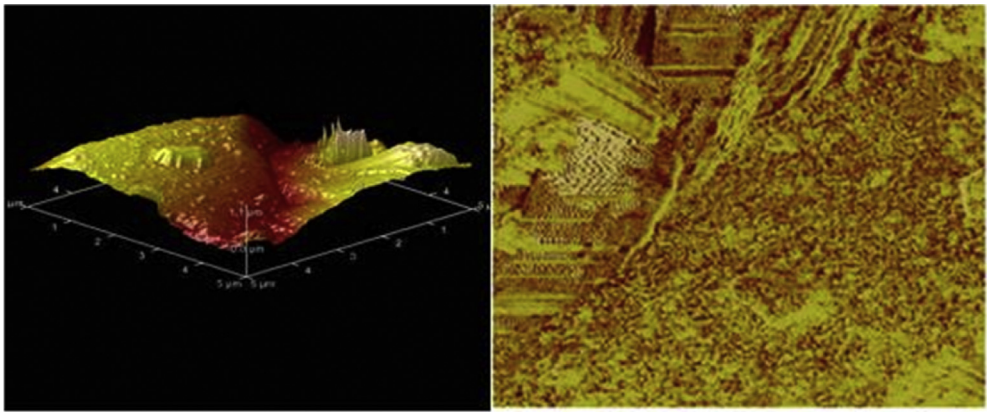

Fig. 3. AFM ofZn–8ZnO–16SiO_2deposited at 1 A/cm^2 for 15 min.

were not observed in the SEM. The coating surface layers play an important role in properties of the mild steel. The better adhesion that occurs within the interface is as a result of the presence of boric acid and the conductance.

Energy dispersion spectrum (EDS analysis) was utilized to determine the composition of the ceramic coating (Figs. 1–2). There is visible different between the EDS of the coating with and without SiO_2 the EDS of the Zn–8ZnO without SiO_2 in the composition revealed Zn and O peaks. While that of the Zn–8ZnO–16SiO_2 showed Zn, O and Si. The development of some primary silicon single crystals in the vicinity of Zn–8ZnO–16SiO_2 composite coating was as a result of the addition of SiO_2 in the bath. This result was in par with the work of [11,12].

Also the Surface topography was studies with AFM measurements to determine the influence of plating parameters on the grain size dimensions, as well as to find out the deposition conditions. AFM was performed on Zn–8ZnO–16SiO_2 composite coating deposition (see Fig. 4). In deposited coating, uniform crystallites coalesced with small grain were found affirming the morphological result obtained from scanning electron micrograph; the topography of the Zn–8ZnO–16SiO_2 composite coating show better adhesion. From Fig. 3, flat, spherical, and hexagonal platelets deposition which indicates SiO_2 dispatches. The growth of spherical crystallites cover the entire surface, thereby giving it a uniform appearance and finer grained texture, dendrites free deposition was obtained.

The XRD pattern of the Zn–8ZnO–16SiO_2 composite coating is shown in Fig. 4. From Fig. 4 it was observed that, the Zn–8ZnO–16SiO_2 coating has five major diffraction peaks of which are: a (45.2°), b (54.4°), c (78.6°), d (93.9°) and e (100.1°), phases at

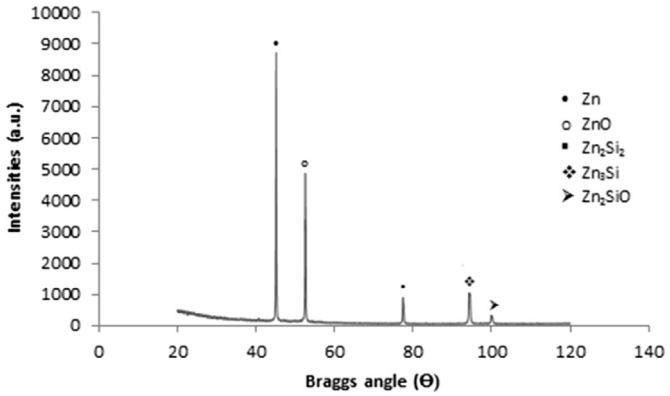

Fig. 4. X-ray diffractive pattern of$Zn-8ZnO-16SiO_2$deposited at 1 A/cm^2 for 15 min.

these peaks are Zn, ZnO, Zn_2Si_2, Zn_3Si and Zn_2SiO. In the diffractogram, one can evidently deduce the crystalline phases of the composite coating material. The X-ray patterns show that there is evident of the Si in the diffractogram. The Zn has the higher peak of all the peaks because of the presence of Zn–8ZnO in the coating. It should be noted that the presence of SiO_2 in the bath can led to interfacial reaction that lead to the formation of Zn_2Si_2, Zn_3Si phases in the composites coating. Similar observation have been made Basavanna et al. [3] on Zn–Ni Alloy coatings.

3.2. Micro-hardness behaviour of the fabricated coating

The hardness values of the metallic-coating before and after thermal treatment are showed in Fig. 5. From Fig. 5 it was observed the microhardness raise with increase of the SiO_2 in the bath from 0 to 16wt%. It can be attributed to the higher hardness of SiO_2 ceramic coating compared to mild steel. The hardness of composite coating strongly depends on the hardness of the SiO_2 which showed that the higher the amount of the ceramic coating the higher the hardness values e.g average hardness value of 142.5HV and 251.2HV were obtained for the 0 and 16wt% SiO_2 in Zn–8ZnO composite coating respectively similar observation has been reported by Refs. [11,12].

As far as hardening behaviour of the composites is concerned, particle addition in the matrix alloy increases the strain energy in the periphery of the particles in the matrix and these tendencies may be due to the formation of the dislocation at the boundary of the ceramic particles by the difference in the thermo-expansion coefficient between the matrix and ceramic particles. On the other point of view the difference between coefficients of thermal expansion of ceramic coating and metal alloy may result in stress concentrations, thus high density of dislocations; the hardness values of the mild steel increases accordingly. These confirm the obvious effect of ceramic coating on strengthening of composites. In general SiO_2 contribute immensely to the hardness behaviour of Zn–8ZnO coatings and hence the absence of cracks and defect as earlier stated is a requirement to produce a well adhered coating with good hardness properties.

3.3. Wear properties of composite coating

It was observed that the composites coating exhibited significantly higher wear resistance than the Zn–8ZnO matrix due to the addition of SiO_2 which acts as a load bearing constituent. As the percentage of SiO_2 increases, the wear rate of the composite coating decreases. Increase in SiO_2 in Zn–8ZnO coating of mild steel restricts the deformation of the matrix material with respect to load, hence the wear rate for higher percentage of composite coating is lower (see Fig. 6) e.g wear rate of 0.006 g/min and 0.001 g/min were obtained for the 0 and 16wt% SiO_2 in Zn–8ZnO composite coating of mild steel respectively.

The decrease in wear rate of the composites coating may also be attributed to higher load bearing capacity of hard SiO_2 material and better interfacial bond between the particle and the matrix reducing the possibility of particle pull out which may result in lower wear. The improvement in wear resistance accompanying the presence of ceramic particles in the Zn–8ZnO of mild steel is due to an increase in average hardness values (see Fig. 5). This has been confirmed by Basavanna et al. [3] for electrochemical Studies of Zn–Ni Alloy Coatings from Acid Chloride Bath. The $Zn-8ZnO-16SiO_2$ coating of mild steel is expected to bear a substantial fraction of the load imposed on the material during the test. The protruding hard SiO_2 ceramic particles will act as micro-cutter for the counter body [9–11].

3.4. Corrosion behaviour studies

The vulnerability of the developed ceramic coating on mild steel to corrode in the 3.65% NaCl was carried out. Table 3 and Fig. 7 showed the corrosion rate, while Fig. 8 showed the coating efficiency of the $Zn-8ZnO-16SiO_2$ ceramic coating of mild steel respectively. From the results obtained in Table 3 and Fig. 7, the corrosion rate of the samples generally decreases as the wt% of SiO_2 increased from 0 to 16. The Zn–8ZnO sample has the higher corrosion rate due to lack of surface protection of SiO_2. This was

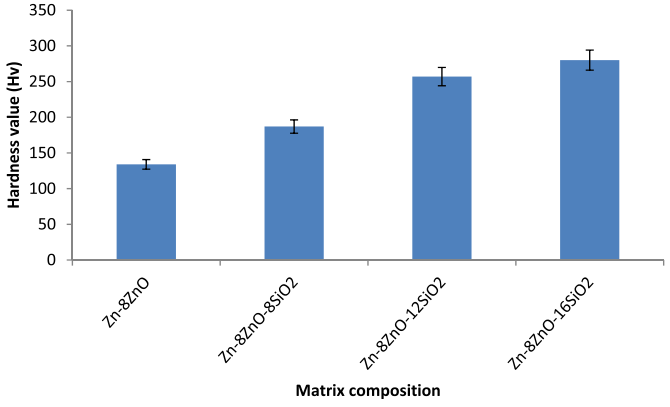

Fig. 5. Micro-hardness of deposited composite coatings prior heat treatmentat 1 A/cm^2 for 15 min.

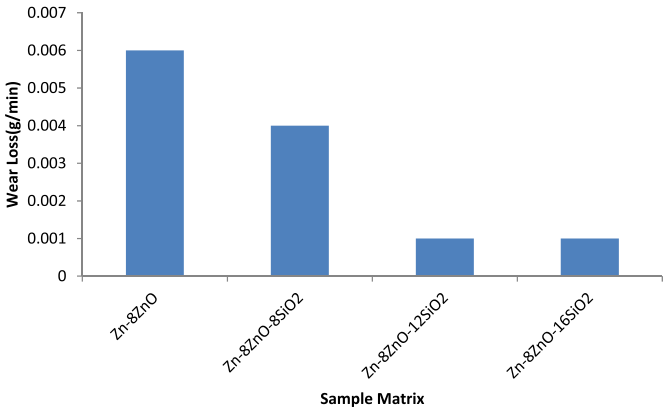

Fig. 6. Wear loss variation of the fabricated coatings.

Table 3
Shows the tafel extrapolation data of the co-deposited alloy.

Coated sample matrixes	E_{corr} Obs (V)	j_{corr} (A/cm^2)	CR (mm/year)	Rp (Ω)
Zn–8ZnO	−1.3541	0.00028	0.13088	642.47
Zn–8ZnO–8SiO_2	−1.3884	0.00281	0.85173	556.34
Zn–8ZnO–12SiO_2	−1.1411	0.00014	0.00422	1411.6
Zn–8ZnO–16SiO_2	−1.0917	4.00E-06	0.00122	3218.8

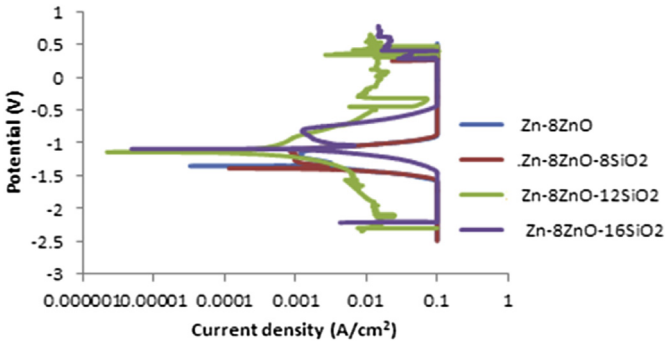

Fig. 7. Shows the linear polarization behaviour of the fabricated composite alloy in 3.65% NaCl.

attributed to the high anodic potential reached by the sample [12]. Meanwhile, Zn–8ZnO–16SiO_2 coated mild steel showed a good decrease in corrosion rate which may be due to the formation of very thin film, which retarded the ingress of chloride ions fully into the plated region and down to the substrate. But, it is good to know that mild steel displayed highest corrosion rate than all deposited samples, Also wt% SiO_2 particulate contribute immensely to the corrosion behavior of Zn–8ZnO coatings and hence the absence of cracks and defect is a requirement to produce a well adhered coating. Hence there was a decreased in the corrosion rate e.g corrosion rate of 0.13088 mm/year and 0.00122 mm/year were obtained for the 0 and 16wt% SiO_2 in Zn–8ZnO composite coating of mild steel respectively.

From Fig. 8, it can be seen that the coating efficiency of the Zn–8ZnO ceramic coating increased with an increases in the wt% of SiO_2. The general increase in coating efficiency with increases in the wt% of SiO_2 is attributed to the good interfacial bonding of the composites coating of the mild steel. The presence of SiO_2 in the coating improved its coating efficiency greatly. It can also be explained that the increase in coating efficiency with increase of

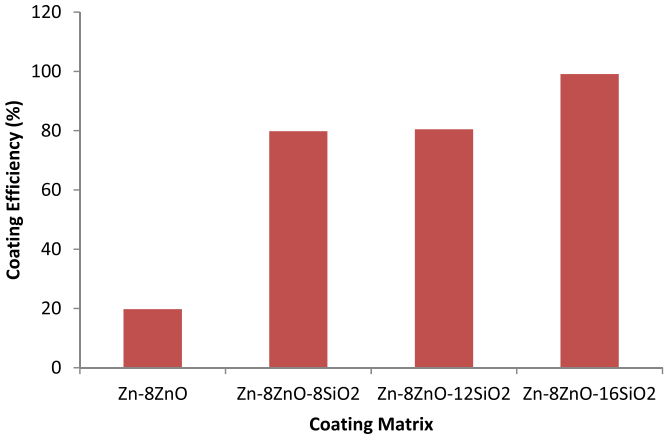

Fig. 8. Computation of the % coating efficiency from PP-PR tafel plots.

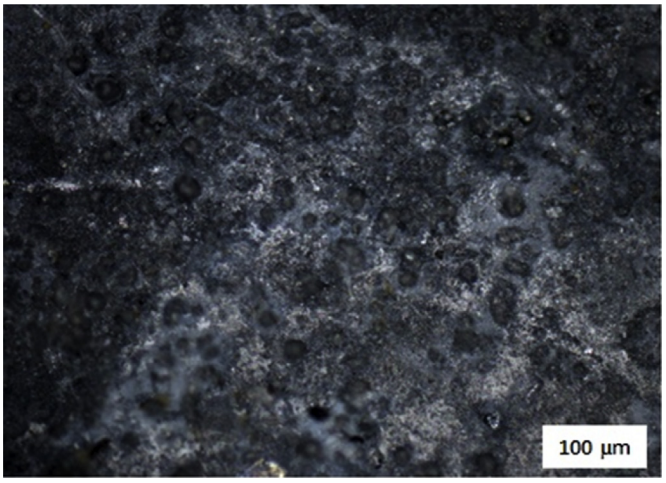

Fig. 9. Shows the morphology of the corrodedZn–8ZnOalloy in 3.65% NaCl.

the coating over the mild steel surface led to the blocking of the active sites, in which direct salt attacks decreased and hence protect the metal from corrosion.

The SEM images were recorded to establish the interaction of coating with metal surface. Figs. 9–10 represents the SEM images of Zn–8ZnO and Zn–8ZnO– 16SiO_2 coating The SEM images revealed that the specimen coated with Zn–8ZnO– 16SiO_2 have a better condition having a smooth surface while the sample coated with Zn–8ZnO is rough covered with corrosion products and appeared like full of pits and cavities.

In the case of Zn–8ZnO– 16SiO_2 sample, one can observed less number of broken particles with less corroded debris formation, whereas in the Zn–8ZnO sample (see Fig. 9), de-bonding and great corroded damage can be seen. In the Zn–8ZnO– 16SiO_2 composite coating samples, as it contains a combination of hard and soft phases, severity and extent of damage on the specimen surface becomes less, in the softer regions as noticed owing to the presence of hard SiO_2 phase. As the hard phases/regions offer resistance to the damaging action of the corrosion, less of the damage was noticed in these systems. The SEM image amply demonstrate greater occurrence of corrosion debris that includes broken particles when system was subjected to corrosion. Thus this observation lends credence to the contention that the presence of SiO_2 phase allows less corrosion of the samples.

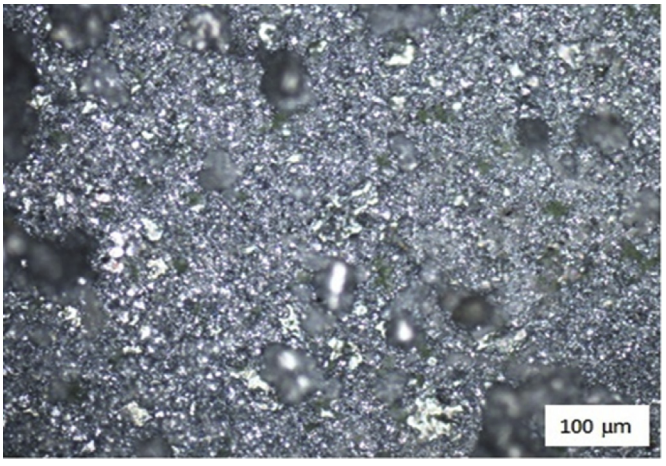

Fig. 10. Shows the morphology of the corrodedZn–8ZnO–16gSiO_2alloy in 3.65% NaCl.

4. Conclusions

After vivid study of deposited Zn–8ZnO–SiO_2 phase on the mild steel, the performance evaluation was systematically observed and a homogeneous and coherent surface morphology was maintained. Based on the results and discussion above the following conclusions can be made:

1. The Zn–8ZnO–SiO_2 coatings showed better adhesion strength compared to the Zn–8ZnO coating.
2. All the properties improved by increasing the SiO_2 in the bath from 0 to 16wt% in the Zn–8ZnO bath.
3. In this work, mixed matrix of Zn–8ZnO–16SiO_2 showed better corrosion resistance as compared to the rest of the matrixes.
4. Uncoated mild steel has been found to be unsuitable for use in chloride contain water due to its relatively high corrosion rate. The electroplated Zn–8ZnO–SiO_2 sample was able to protect mild steel in chloride medium to retard corrosion attack.
5. The addition of hard SiO_2 particles to Zn–8ZnO coating of mild steel can be used to improved the properties of mild steel

Acknowledgement

This material is based upon work supported financially by the National Research Foundation. The equipment support by Surface Engineering Research Centre (SERC) Tshwane University of Technology, Pretoria is deeply appreciated.

References

[1] D. Fullston, Zinc coating thickness effects on hot dip galvanized steel corrosion rates At A severe marine site, Corros. Mater. 29 (2004) 165–167.
[2] O.S.I. Fayomi, A.P.I. Popoola, An investigation of the properties of Zn coated mild steel, Int. J. Electrochem. Sci. 7 (2012) 6555–6570.
[3] S. Basavanna, Y. Arthoba Naik, Electrochemical studies of Zn–Ni Alloy coatings from acid chloride bath, J. Appl. Electrochem. 39 (2009) 1975–1982.
[4] C. Mou, X. Sen Sen, Y. Ming, Electro-deposition behavior of Mg With Zn from acidic sulfate solutions, J. Solid State Electrochem. 14 (2010) 2235–2240.
[5] B.M. Praveeen, T.V. Venkatesha, Electro-deposition and corrosion resistance properties of Zn-Ni/Tio2 nano composite coating, Int. J. Electrochem. 261 (2011) 407–792.
[6] A.P.I. Popoola, O.S.I. Fayomi, Performance evaluation of zinc deposited mild steel in chloride medium, Int. J. Electrochem. Sci. 6 (2012) 3254–3326.
[7] O.S.I. Fayomi, V.R. Tau, A.P.I. Popoola, B.M. Durodola, O.O. Ajayi, C.A. Loto, O.A. Inegbenebor, Influence of plating parameter and surface morphology on mild steel, J. Material And Environ. Sci. 2 (3) (2011) 271–280.
[8] N.S. Patel, S. Jauhariand, G.N. Mehta, S.S. Al-Deyab, I. Warad, B. Hammoouti, Mild steel corrosion inhibition by various plant extract in 0.5 M sulphuric acid, Int. J. Electrochem. Sci. 8 (2013) 2635–2655.
[9] A.E. Refaey, W. Tillmann, Characterization of titanium/steel join brazed in vacuum, J. Weld. Res. Counc. 87 (2008) 113–118.
[10] G. Fontana, M: Corrosion Engineering, third ed., Mcgraw Book Company Publishers, Singapore, 1987, pp. 134–147.
[11] C. Mohankumar, K. Praveen, V. Venkatesha, K. Vathsala, O. Nayana, Electro-deposition and corrosion behavior of Zn–Ni and Zn–Ni–Fe2o3 coatings, J. Coat. Technol. Res. 9 (1) (2012) 71–77.
[12] A.E. Elsherief, M.A. Shoeib, Characterization of electrodeposited Zn-Ni alloy from an all-chloride solution, Corros. Prev. Control 50 (2003) 25–30.
[13] S.K. Tiwari, R.K. Sahu, A.K. Pramanick, S. Raghuvir, Development of conversion coating on mild steel prior to sol gel nanostructured Al_2O_3 Coating For Enhancement Of Corrosion Resistance, Surf. Coatings Technol. 205 (2011) 4960–4967.
[14] M. Masao, T. Seiya, H. Tetsuji, Fabrication of Tial3 coating on tial-based alloy by Al electro-deposition from dimethylsulfone bath and subsequent annealing, Surf. Coatings Technol. 205 (2011) 5141–5146.
[15] N. Pedro De Lima, N. Adriana, P. Correia, S.A. Walney, Corrosion study of electrodeposited Zn And Zn-Co coatings in chloride medium, J. Braz. Chem. Soc. 18 (2007) 1164–1175, 174.
[16] T. Dikici, O. Culha, M. Toparli, Study of the mechanical and structural properties of Zn–Ni–Co ternary alloy electroplating, J. Coat. Technol. And Res. 7 (6) (2010) 787–792.
[17] L. Chuen-Chang, H. Chi-Ming, Zinc-nickel alloy coatings electrodeposition by pulse current and their corrosion behavior, J. Coat. Technol. And Res. 3 (2) (2006) 99–104.