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Abstract	Surface modification is known to contribute immensely to the properties of alloys. The motivation behind this present study is to develop a bath with quality coating with targeted $Zn–SnO_2$ reinforced Zn-based

composite particulate produced by electrolytic co-deposition route. The influence of SnO_2 on $Zn–13SnO_2$ sulphate electrolyte on the properties of the nano-particulate coatings was investigated. SnO_2 was varied from 0 to 16 wt%. The microchemistry and interfacial structural properties were tested by X-ray diffraction (XRD), optical microscope, scanning electron microscope (SEM) equipped with energy disperse spectrum (EDS). The corrosion degradation properties in 3.65 % NaCl static solution at 40 °C were characterized by high-resolution optical microscope (HR-OPM). The structure of the conditioned composite coating indicates the presence of thin blend phase of $ZnSn_2$, Zn_2Sn and Zn. The microstructure revealed good distribution of particulate within the interface. The corrosion rate results properties shows 0.007786 mm/ year for Zn–7Sn–0.3 V–S. The study has established that up to 13 wt% SnO_2 particulate in bath on mild steel can be used in improving the structural and corrosion resistance of mild steel.

Chapter 23
The Study of the Microstructure and Interfacial Reaction of Binary Composite Coating

Ojo Sunday Isaac Fayomi, Abimbola Patricia Idowu Popoola and Cleophase Akin Loto

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Keywords Interfacial effect · Microstructure · Electrochemistry · SEM

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23.1 Introduction

The usage of zinc coating for industrial application is enormous. It is considered as one of the versatile methods of protection of steel. Coatings over years have been known to exhibit excellent susceptibility to mechanical and corrosion resistance in harsh medium [1–4]. Although cyanide, non-cyanide, alkaline and acidic bath are known to be associated with pollutant, chloride and sulphate solution even in their admixed state have been gaining much importance with their exceptional characteristics. Meanwhile, zinc services life depreciates drastically in a more severe and high temperature environment due to the existence and formation of corrosion product [5–7].

Invariably excellent surface modification and coatings depend on the kind of bath formulation and constituents. Complexing agents contribute immensely to the coating activities which simultaneously depend on the pH, the ions of the individual particulate, temperature and other parameters. In view of this, production of single deposit alloys with quality deposits is essential for good coating resistance.

Nanocomposite materials which consist of grain and metal matrix possess good characteristics to be developed as new materials that are novel in nature [6–12]. From the literature, several studies on zinc coating have been carried out over decades but the focus of the authors defers. Popoola and Fayomi [10] attempted to increase the corrosion behaviour of mild steel by depositing SiO_2 into the zinc matrix. Lin and Huang [9] worked on pulse current electrodeposition of zinc–nickel alloy on steel. Kanagalasara and Thimmappa [7] evaluated $Zn–ZrO_2$ progression in bath in an attempt to improve the surface properties of steel for better performance. The coated layer is extremely bound to the steel substrate with good microstructure due to proper optimum process parameter and additive inclusion. Studies on zinc coating are ever unending due to the unique properties it gives.

However, in an attempt to further consider possible advanced material, SnO_2 was inoculated on the Zn-based bath formation leading to binary induced co-deposited Zn–Sn films. Subsequently, the present research was aimed in evaluating the effect of process variable on the electro-oxidation stability and strengthening behaviour of $Zn–SnO_2$ interface.

23.2 Experimental Procedure

The dimension of the mild steel (substrate) sheet used was 40 mm × 20 mm × 1 mm and zinc sheets of 30 mm × 20 mm × 1 mm were prepared as anode electrodes. The mild steel specimens' chemical composition is shown in Table 23.1.

The cathode was mild steel. The mild steel specimens were polished mechanically, degreased and rinsed with water. The initial surface preparation was performed with the fine grade of emery paper, properly cleaned with sodium carbonate, degreased/pickled and activated with 10 % HCl at ambient temperature, then

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Table 23.1 Nominal chemical composition (wt%) of mild steel substrate

Element	C	Mn	Si	P	S	Al	Fe
% composition	0.15	0.45	0.18	0.01	0.031	0.005	Balance

Table 23.2 Summarized data of deposited samples for $Zn–SnO_2$ sulphate bath formulation

Composition	Mass concentration (g/L)
Zn	75
K_2SO_4	50
Boric acid	10
SnO_2	7–13 g
$ZnSO_4$	75
pH	4.8
Voltage	0.3–0.5 V
Time	20 min
Temp	40 °C

Table 23.3 Itinerary bath composition of binary $Zn–SnO_2$ sulphate alloy co-deposition

Sample order	Material sample	Time of deposition (min)	Potential (V)	Current (A/cm^2)
Blank	–	–	–	–
Sample 1	$Zn–7SnO_2–0.3$ V–S	20	0.3	2
Sample 2	$Zn–7SnO_2–0.5$ V–S	20	0.5	2
Sample 3	$Zn–13SnO_2–0.3$ V–S	20	0.3	2
Sample 4	$Zn–13SnO_2–0.5$ V–S	20	0.5	2

followed by instant rinsing in deionized water. The prepared Zn–Sn composite as stipulated in Tables 23.2 and 23.3 was periodically stirred to obtain a homogeneous solution before electrolytic deposition process. The cathode was made of mild steel and the anode used of commercially of 99.99 % pure zinc was obtained from Surface Engineering Research Centre Laboratory, Pretoria, South Africa. The bath was prepared a day prior to the plating test. SnO_2 (50 nm) nanoparticles added to the bath were kept in suspension for 12 h using a magnetic stirrer to prevent unnecessary agglomeration of the particulate in the medium. The pH of the bath was kept constant at 4.8 and adjusted with addition of HCl and NaOH. The prepared cathode and anodes were connected to the D.C. power through a rectifier at a current density of 2 A/cm^2. With varying applied voltage of 0.3 and 0.5 V for dwell time of 20 min and stirring rate of 100 rpm, all the experiments were conducted at ambient temperature.

23.3 Characterization of the Coated Composite

The structural evolution was characterized on Joel JSM6510 scanning electron microscope (SEM) built with energy dispersive spectroscopy (EDS) and Olympus BX51M optical microscope (OM). The X-ray diffraction (XRD) appearance was extrapolated from Rigaku/Dmx 2200 pc automatic X-ray diffractometer with Cu target K_α radiation to identify the phase change.

23.4 Electrochemical Studies

Linear potentiodynamic polarization technique was used to investigate the corrosion properties of the coating. The electrochemical studies were performed with Autolab PGSTAT 101 Metrohm potentiostat/Galvanostat using a three-electrode cell assembly in a 3.65 % NaCl static solution at 40 °C. The anodic and cathodic polarization curves were recorded by a constant scan rate of 0.012 V/s which was fixed from ±1.5 mV. From the Tafel corrosion analysis, the corrosion rate, potential and the linear polarization resistance were obtained. The coated samples were used as working electrode with exposed surface area of 1 cm^2. Nova 1.7 was used to extrapolate the corrosion propagation obtained from the Tafel curves.

23.5 Results and Discussion

23.5.1 Structural Studies

Figure 23.1 shows the morphological structure of the mild steel substrate and Zn–SnO$_2$ coating. The surface morphologies of the Zn–SnO$_2$ sulphate deposited mild steel coatings developed at different applied voltages with variation of additives were investigated. The influence that the composite particles incorporated was felt. It can be seen that the structure comprised of dispatched shaped crystallites of various compactable sizes. More so coating structure is observed to be more adhered with Zn–13Sn–S–0.5 V matrix. It is important to note as mentioned by researchers [3, 4] that composite particle has a strong effect on the deposit surface structure which is caused by the changes in deposition mechanism. The nucleation and the proportion of growth could be attributed to the current density and potential which is in line with that observed in the literature [5]. The non-porous nature of the deposited coating indicated in Fig. 23.1b shows the potent capacity of Sn ions distributed within the Zn bath interface. The build-up resulting into slight regularity of the crystal was in accordance with opinion [1, 2] that some atoms in sites inhibit crystal growth at a particular location; hence the crystal growth due to inhibition and remaining plane developed preferred orientation as a function of slow rate of deposition.
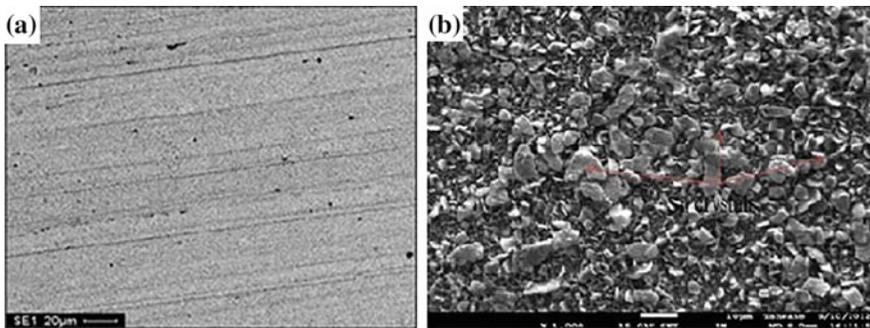
Fig. 23.1 SEM showing the surface morphology of **a** mild steel substrate **b** Zn–13Sn–0.5 V chloride deposited sample
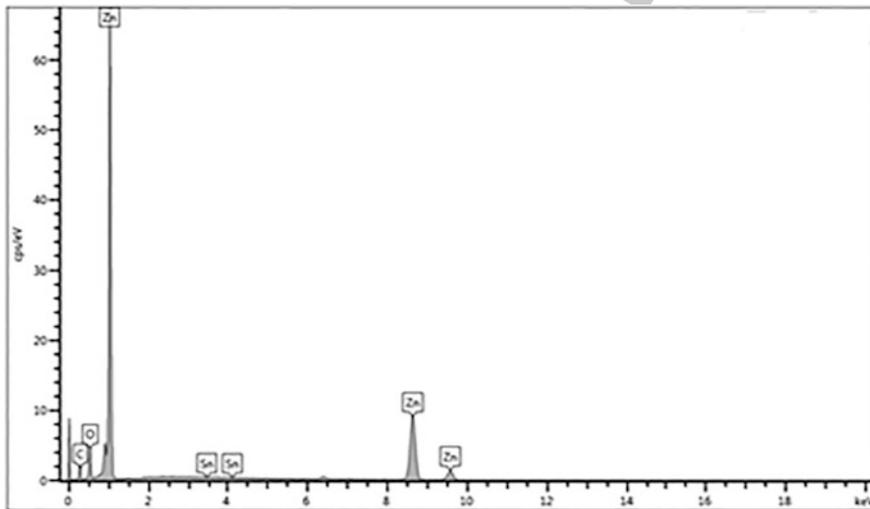
Fig. 23.2 EDX micrograph of Zn–13Sn–0.5 V sulphate deposited sample

In order to attest to the existence of the admixed composite, an elemental EDX quantification was employed as shown in Fig. 23.2 with Sn and Zn content at the interface. The resultant elemental composition from the EDS correlates with the morphological dispersed film physically observed in the study. Likewise, the improvement of different crystal structures can be related to the growth of grains due to its compactness.

Fig. 23.3 Potentiodynamic polarization curves for Zn–Sn sulphate deposited mild steel
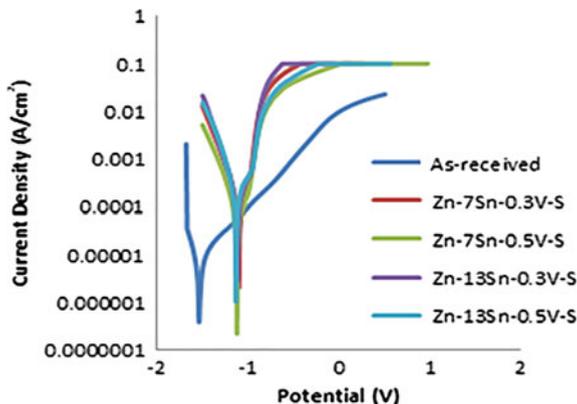

23.5.2 Corrosion Studies

The electrochemical oxidation properties of the $Zn–SnO_2$ sulphate coatings were examined using a linear potentiodynamic polarization testing method. For quantitative studies the immersion was done in 3.65 % NaCl and the polarization curve is illustrated in Fig. 23.3. The potential of the entire as-coated composite alloy was observed to shift towards positive values for all the samples except for the substrate that moves drastically towards more negative region. The negative shift of the potential indicated the strong dissolution of the mild steel films due to the absence of passivation [10]. It is significant to mention that the positive shift of the potential indicates the formation of protective film and an increase in the passive film thickness. Among the composite deposited sample, Zn–7Sn–S–0.3 V exhibited a more stable passivity than the other coatings due to the large number of tiny particles deposited on the cathode surface at higher applied voltage.

In addition, it was also observed from the curves that the corrosion rate of Zn–7Sn–S–0.3 V alloy coating decreases with the presence of Sn in the deposit for all samples. The effect of the composite particle on the structural behaviour helped to improve corrosion resistance; which is against the literature findings [12, 13] that stated that the microstructure of the deposited coating had less effect on corrosion resistance.

From the polarization results (Table 23.4), mild steel was found to exhibit highest corrosion current density of 7.04×10^{-2} A/cm^2 than all deposited samples, while Zn–7Sn–S–0.3 V had I_{corr} of 1.87×10^{-5} A/cm^2; a three order magnitude

Table 23.4 Summary of the potentiodynamic polarization results of Zn–Sn

Sample	I_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (mm/year)
As-received	7.04E−02	−1.53900	4.100000
Zn–7Sn–0.3 V–S	1.87E−05	−1.09955	0.007786
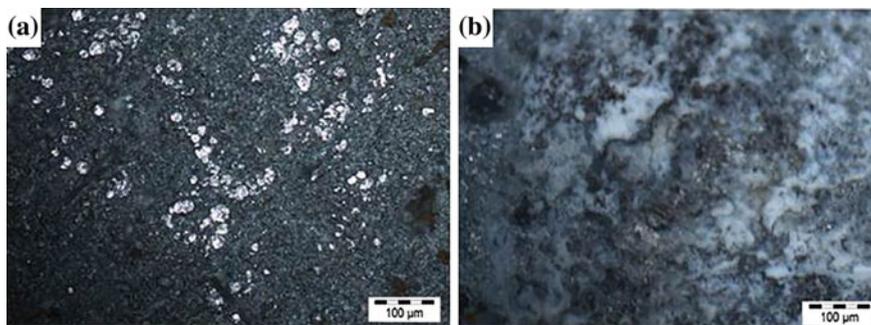
Fig. 23.4 Optical micrograph of the morphology for Zn–13Sn–0.5 V sulphate deposited **a** before corrosion and **b** after corrosion

decrease in corrosion current density was attained due to the effects of alloy composition electrodeposited on mild steel. Polarization resistance (R_p) for Zn–7Sn–S–0.3 V is 5.64×10^3 Ω which was the highest attained for all coated samples in this matrix. Three orders increase in magnitude was attained when compared with 2.76×10^2 Ω for the as-received sample.

Optical microscope was used to observe the post-corrosion morphology of Zn–SnO_2 before and after corrosion. In general, no obvious pitting was observed. The stability of the coated alloy at this harsh environment might be due to the existence of the passive film layers (Fig. 23.4).

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23.6   Conclusions

After critical investigation of the deposition of the Zn–SnO_2 alloy phase on the mild steel substrate, the trend of coating performance was examined and a coherent structure was identified. Based on the evaluation of the results and discussion, the following conclusions can be made:

- After successful co-deposition, it was observed that adding a small percentage of SnO_2 particles into the sulphate bath improved the microstructural properties of the Zn–Sn alloy. The Sn ions dissolve homogeneously and further increase the oxidation resistance of the Zn–SnO_2 alloy.
- Bright and cohesive Zn–Sn alloy surfaces were fabricated from bath containing equimolar average ratio of Sn^{2+}/Zn^{2+} without brightener.
- The electrochemical study revealed that corrosion resistance of mild steel was significantly improved after zinc–tin deposition. The increase in corrosion resistance of the entire composite is especially due to the formation of high Sn alloy phase.

- The uncoated substrate has been seen to be actively unstable for use in active simulated environment because of the corrosion rate trends. However, with the Zn–SnO$_2$ alloy formation, formidable protection against excessive corrosion challenge was reduced dramatically.
- Invariably, the addition of SnO$_2$ particulate into zinc on mild steel can be used to improve the properties of mild steel.

AQ4

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