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Influence of Composite Nano Coating on Ternary Sulphate Co-deposition: Corrosion and Surface Characterization

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Abstract

In this study, composite Zn-ZnO-MgO have been produced from a sulphate bath in the presence of dispersible MgO nano composite on mild steel substrate in the absence of surfactant. The resulting fabricated coating shown that the amount of MgO embedded in the coating is dependent not only on the time of deposition but also the incorporated particulate and the applied current density. The influence of the particulate from 8-16 wt% on the ternary series was extensively investigated on the coating efficiencies and coating texture. The structural changes of the co-deposited alloys were investigated by scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS). The corrosion characteristics properties in 3.65% NaCl medium were studied using linear potentiodynamic polarization route and characterized by high resolution optical microscope. Results show the deposition of MgO particulate contribute immensely to the corrosion propagation resistance of the Zn-ZnO-MgO coating. It was also established that the addition of the dispersible composite significantly influence the coating texture and efficiency.

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Keywords: Ternary coating, Particulate, Electrochemical characteristics, Coating efficiency

1. Introduction

The global uses and enormous demand of mild steel among other metals are due to low cost and its availability for the manufacturing of engineering components. One of the major weaknesses of mild steel is its structure

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properties and poor corrosion behaviours [1-2]. Due to these shortcomings, mild steel protection techniques have been carry out to improve the lifespan of steel against deterioration.

Electrodeposition of metals has become a phenomena used in many industries to persevere chemical deformation. The major advantage of electrolytic co-deposition is its barrier thin film coatings [3-4]. Taking into account all these considerations, zinc coatings and zinc-based coatings are used broadly to protect steel [5-6]. Investigation in the zone of zinc deposition on mild steel are quite unending because of the unique properties and the very low cost it offers [7].

The addition of additives in plating bath especially composite influences the structural characteristics and reduce porosity in other side gives good protection in corrosion resistance properties [8]. The electrolytic co-deposition of inert particles and metals is a very complex process. The quality of a coating depends on many factors besides the nature of the materials involved, the process parameters such as the control of the pH, the stirring rate, the distance between the anode and cathode and the nature of induced bath formulation (chloride/sulphate bath) [9].

Micron/Sub-micron sized particles of ZnO were reported to be easily co-deposited into Zn matrix better than their nano-sized counterparts [9-10]. Hammami et al. studied the inclusion of MgO nanoparticles into Zn matrix and the produced composite alloy exhibited high corrosion resistance, and better structural stability [10]. Therefore, in this study, reports on the development and fabrication of Zn nanocomposite coatings reinforced with nano-sized ZnO and MgO particles are attempted to provide solution to corrosion performance over steel.

2. Experimental Procedure

2.1. Material preparation

Flat carbon steel samples obtained from Owode Onirin market, Lagos, Nigeria was cut into 40 X 20 X 3 mm dimension with the chemical composition presented in Table 1. The substrate which is the steel contains 99.98 % Fe and anodes used contain 99 % pure zinc. Analar grade chemicals were used. Deionized water was used for preparation of the electroplating bath solution. From then on, the surface preparation of the mild steel sample was prepared with different grades of emery paper in the order of 60 μm, 120 μm, 400 μm, 800 μm and 1,600 μm to render free of defects. Samples were activated by dipping in 2M HCl solution at room temperature for 15 seconds followed by rinsing in distilled water as described by [4].

Table 1: Chemical composition of the low carbon steel

Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

2.2. Preparation of coating formation

The prepared sample was dipped in a solution containing dissolved bath constituents which was heated for 1hour and simultaneously stirred at 200 rpm to obtain a homogenous solution. Cathode and anodes were connected to the D.C. power supply through a rectifier. Electrodeposition was carried out with applied voltage of 3V for 20 min. With the depth of dipping and distance from cathode to anode kept constant. Immediately after the plating, rinsing was done in distilled water and samples were air-dried. The bath composition and process parameters are shown in Table 2.

Table 2: Bath Composition of Zn-ZnO-MgO coating

Composition	**Mass Concentration (g/L)**
$ZnSO_4$	75
ZnO	30

K_2SO_4	50
Boric Acid	10
MgO	8 -16
$NaSO_4$	75
Glycine	10
Thiourea	10
pH	4.8
Voltage	I Volt
Time	20 min.
Temp.	40°C

2.3. Surface characterization

The surface morphology of the electrodeposits was observed using optical microscope (OPM) at 100μm. The surface texture and coating thickness were also determined using Positector.

2.4. Corrosion testing

AUTOLAB Pontentiostat was used to study the corrosion behavior of as-received sample and the coatings in 3.65 % NaCl environment. The polarization measurements were carried from a start potential of −1.5 to an end potential of +1.5 V at a scanning rate of 0.01 V/s. KCl was used as a reference electrode and graphite served as a counter electrode. Working electrode was the sample, and the whole body of the specimen was exposed to the corrosion environment. From the Tafel corrosion analysis, the corrosion rate and linear polarization resistance were obtained.

3. Results and Discussion

The results obtained for Zn-ZnO-MgO sulphate electro-deposition are shown in Table 3. The morphology of Zn-ZnO-MgO at 8wt% and 16wt% are presented in Fig. 1. From the structural characterization, the mild steel shows plan clean surface without the presence of crystals (see Fig. 1a). On the other hand, there are several dominate crystal growth developed at the interface of the produced coatings without surface defects. With the coating at 16 wt% a visible flake-like crystalline structural pattern was seen at the general interface. The superior microstructure exhibited by the composites can be attributed to the inclusion and uniform dispersion of the nanoparticles in the Zn matrix. Although embedment of nanoparticles in a metal matrix promotes increase in number of nucleation sites [8] and impedes crystal growth resulting in small-nanosized metal grains [10]. Zn-ZnO-MgO showed better microstructures as compared to the mild steel. This might have been caused by the nature of ZnO particles which are very fine and tend to agglomerate when dispersed in solution. Fig. 2 shows the surface (texture) of the coated samples, the results were obtained using Positector. However, the coating texture of Zn-30ZnO-8MgO shows less rough propagation average of 112 inches compare to other coatings in the same series. The highest roughness projection among the developed coating was found with Zn-30ZnO-8MgO at 0.5A/dm^2 lower current density. It is noteworthy to mention that the process parameter influence the structural texture which may alter the performance life of any coating. The incorporation of particles into a metal matrix promotes homogeneity and reduces porosity [8], this was the assertion observed on the effect of embedded particulate on the coating efficiency. The coating efficiency as presented in Fig. 3, follows the same trend of the coating texture in a reverse order. Higher coating efficiency was observed with Zn-30ZnO-8MgO at 1.0A/dm^2 follow by Zn-30ZnO-16MgO-1.0 A/dm^2. Zn-30ZnO-16MgO-0.5 A/dm^2 and Zn-30ZnO-8MgO-0.5A/dm^2

Table 3: Summarized data of Zn-ZnO-MgO plated samples for constant plating time at various current

Sample Labels	Time (min)	Coating Thickness (µm)	Coating Texture (Inch)	Weight Gain (g)	Current Density (A/dm²)	Additive Concentration (g)
As received						
Zn-30ZnO-8MgO	20	420.60	112.0	0.0519	1.0	8
Zn-30ZnO-8MgO	20	409.34	329.0	0.0924	0.5	8
Zn-30ZnO-16MgO	20	332.94	252.4	0.0630	1.0	16
Zn-30ZnO-16MgO	20	313.82	282.5	0.0813	0.5	16

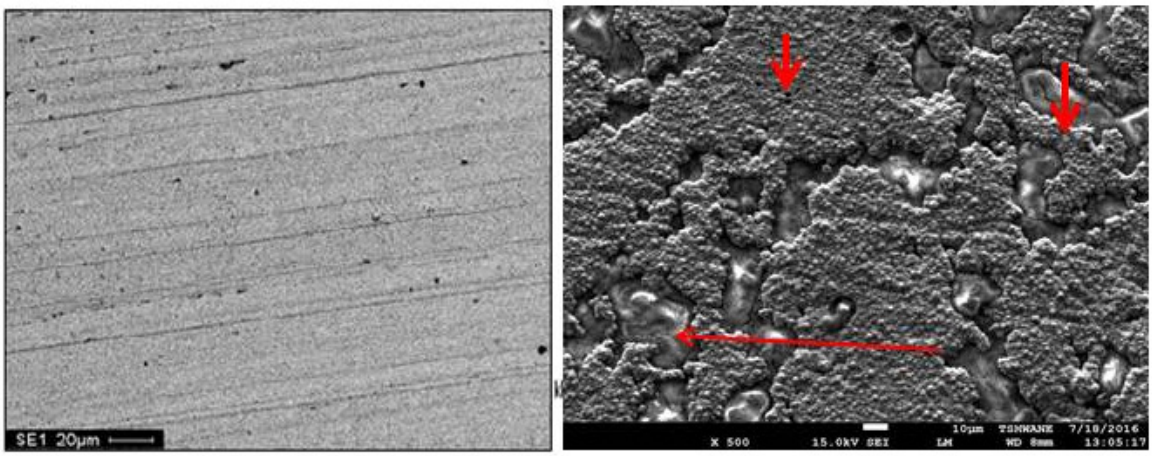

Fig. 1: Micrographs of composite coating of Zn-ZnO-MgO coatings

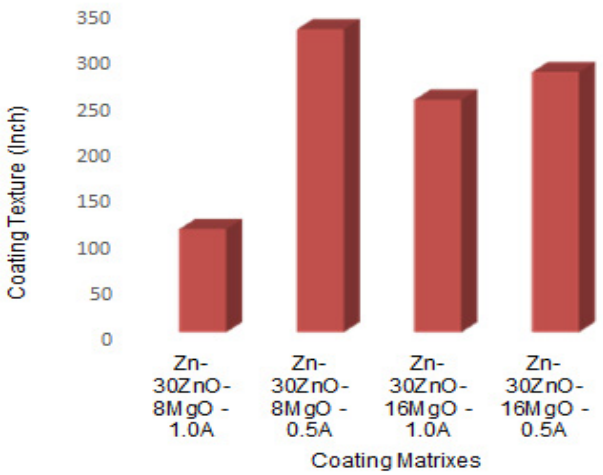

Fig. 1: Coating texture of Zn-ZnO-MgO coatings

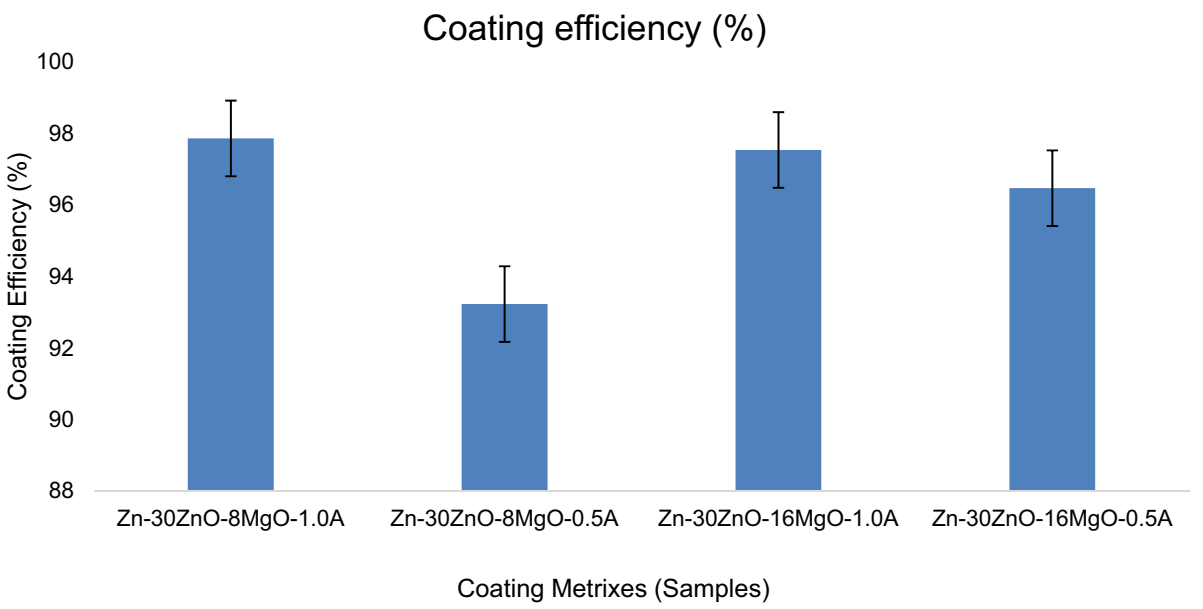

Fig. 3: Micrographs of composite coating of Zn-ZnO-MgO coatings

1.1 Potentiodynamic polarization studies

Fig. 4 shows the polarization curves of as-received and Zn-ZnO-MgO series composite coatings obtained in 3.65 wt% of NaCl environment. A notable positive shift in polarization potential was observed for the coated composite coating as compared to as-received sample. This result shows that the as-received sample had high corrosion rate. It is noteworthy to mention that the inclusion of ZnO and MgO nanoparticles into Zn matrix increased the potential by -0.94400 from -0.30322 V of Zn-16ZnO-8MgO. The increment of these particles in the bath from 8 to 16 g/L yielded no significant results. Nanoparticles incorporated in a metal matrix form inert physical barriers that protect the metal matrix from corrosion attack of the corrosive medium. Therefore, improvement in corrosion resistance of the Zn matrix is owed to the presence of the inert particulates in the coating.

Table 4: Electrochemical corrosion data obtained for Zn-ZnO-MgO plated samples in 3.65%NaCl concentration at 298K.

Sample	I_{corr} (A/cm^2)	R_P (Ω)	E_{corr} (V)	Corrosion rate (mm/yr)
As-received	0.012645	11.812	-0.94400	146.93
Zn-30ZnO-8MgO-1.0A	0.000202	152.56	-0.30322	3.1347
Zn-30ZnO-8MgO-0.5A	0.000855	118.39	-0.35365	9.9404
Zn-30ZnO-16MgO-1.0A	0.000270	145.00	-0.31443	3.6108
Zn-30ZnO-16MgO-0.5A	0.000311	136.08	-0.41510	5.1812

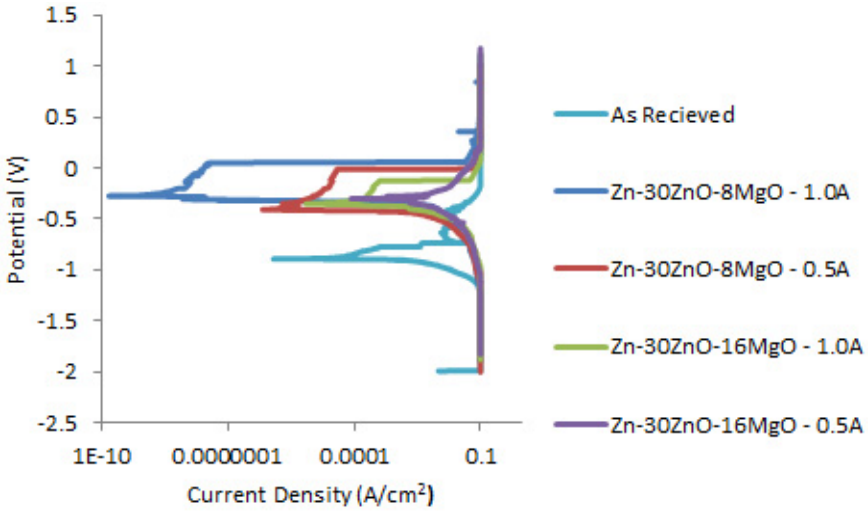

Fig. 4: Potentiodynamic polarization curves for Zn-ZnO-MgO coatings matrix.

4. Conclusion

Zn-ZnO-MgO nanocomposite coatings have been successfully produced by electrodeposition technique. 30 g/L ZnO with 8g/L MgO proved to be the optimum bath loading for improved corrosion resistance.

1. SEM analysis showed that the presence of the nanoparticles in the coating inhibits grain growth and modify crystollographic orientation of Zn matrix.
2. The texture characteristics also show lower resistance propagation especially for the Zn-30ZnO-8MgO-1.0A/dm^2 as a result of interfacial solid precipitation.

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