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Effect of MgO/MnO_2 Additives on the Structural Properties of Zinc Electroplated Mild Steel

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Abstract

Low carbon steel is widely used in engineering applications due to its availability, physical properties and reasonable cost. Regardless of the massive use of mild steel in engineering applications, their application is limited to high tribology and corrosive environment are limited due to low corrosion resistance properties, low microhardness and poor tribological properties. The increase in service life and exceptional properties of reinforcement composite coatings for advanced engineering application has attracted many researchers world-wide. In this study, the effect of manganese oxide (MnO_2) on Zn-MgO chloride bath coating by co-deposition route on mild steel is studied. The coating micrographs and surface thickness were examined by means of scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS) and PosiTector (SPG) respectively. The thermal stability of the synthesized composite coatings studied in isothermal furnace at 350°C. The findings of the studies are discussed in this paper.

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Keywords: Electrodeposition; Low carbon steel; Micro-hardness; Thermal stability; Corrosion behaviour; Rare earth metal (REM)

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1. Introduction

Mild steel is widely used in structural engineering constructions due to its physical properties and it is also less expensive. The use of mild steel is therefore limited due to the conditions application used [1].

These conditions can lead to the deterioration of the metal surface by corrosion or application conditions like wear intensity [2-4].

Electrodeposition is a surface engineering technique used enhance the properties of metals like mild steel due to their restriction to advanced applications [5-7]. Deposition method is known to be cost effective and efficient methods of developing Zinc coatings, which is advantageous as it enables the controlling of the deposit thickness and room temperature working conditions. Enough evidence from literature reports that composites coatings of desired properties can be developed by using various deposition parameters [8,9]. The metal coating deposited on the surface should bear desired characteristics and properties. The properties that can be enhanced by electrodeposition includes corrosion resistance, surface hardness, wear resistance and surface morphology. Electrodeposition also comes in hand for decorative purposes [10]

Electroplating of Zinc onto mild steel has been considered as one of the main methods used for the corrosion protection of steel used in industrial application. This process of sacrificial protection owes its success to the high electronegativity of Zinc. Zinc deposition using the chloride process offers a number of advantages like superior brilliance and levelling, high plating efficiency range of 95 – 100% [4,11]

In the recent studies, there has been the development of novel composite coatings containing nanoparticles that can be carbides, metal oxides etc. The nanoparticles usually have some beneficial effects like good microhardness and corrosion resistance properties on the substrate. Recent research have proven that metallic composite coatings indicates that nanoparticles used in their oxide form are very promising dopants for material coatings to be used in advanced applications [5]. In the present study, Electrodeposited Zn-MgO/MnO_2 composite coating on low carbon steel is studied. The focus of the study is its microstructural evolution, anticorrosive and mechanical properties of the deposited composite coatings.

2. Methodology

Mild steel (substrate) was cut to 40 mm x 20 mm x 1 mm sheet were polished mechanically with fine grades of sand papers, degreased and immediately water washed before electrodeposition. The zinc anodes sheets (99.99% pure) of 30 mm x 20 mm x 1 mm were used. Table 1 below represent the chemical spectrum of the used low carbon steel.

Table 1: Chemical composition of low carbon steel sample

Element	C	Mn	Si	P	S	Al	Ni	Fe
Wt %	0.18	0.45	0.18	0.01	0.031	0.005	0.008	99.19

The prepared mild steel substrate surface was activated in 10% HCl solution for 10 seconds and rinsed in deionised water. Analar grade chemicals were utilized to prepare the electrodeposition solution. The solution was then heated to 40°C to mix and promote dissolution of any lumps that may have formed in the bath solution. The bath produced was stirred continuously using a magnetic stirrer. Table 2 and table 3 below represent the bath formulation and electrodeposition parameters respectively.

Table 2: Bath composition of Zn-MgO-MnO_2 ternary co-deposition

Composition	Mass concentration (g/L)
ZnCl	100
MgO	20
MnO_2	6-18
KCl	40
Boric Acid	20
Glycerin	20

Table 3: Electroplating parameters

Parameters	
Time	15 minutes
Voltage	2.5 V
Current Density	1.5 A
Temperature	40ºC

The surface morphology of the developed coatings was characterized by means of SEM/EDS. The optical microscope (OPM) was also used to evaluate the morphological properties of the synthesized coatings after heat treatment.

3. Results and discussion

Experimental results obtained for Zn-MgO/MnO_2 deposition coatings are presented in table 4. The deposition voltage was kept constant during the experiment. Following the Zn-MgO/MnO_2 deposition, good surface coatings were achieved at high MnO_2 content.

Table 4: Electroplating pattern

Sample identification	Additive composition	Deposition time (Min)	Potential (V)	Current Density (A/cm^2)
Sample 1	Zn-MgO	20	2.5	1
Sample 2	Zn-MgO-6MnO_2			
Sample 3	Zn-MgO-12MnO_2			
Sample 4	Zn-MgO-18MnO_2			

3.1 Thickness Analysis

From figure 1, the results show that there was a general increase in the thickness of the plated samples as MnO_2 was added up to a mass of 12g. A decrease in the thickness of plated sample is noted as the amount of MnO_2 is increased to 18g. Although there is a decrease in the plating thickness on the 4^{th} sample, it can be seen that the thickness is still bigger than that of sample1 and sample 2. A small difference of 0.0057 inches in the thickness can be noted between sample 2 and sample 3.There is a bigger difference of 0.0912 in the thickness between sample 1 and sample 3.

3.2 Morphological Analysis

Figure 2(a)–(d) above shows the micrographic structures of the coatings with the addition of MnO_2. The micrograph (a) shows a homogeneous and defect free coating. A homogeneous interface can also be noticed on micrograph (b) and (c) but with decreasing crystal particle size. This can be due to the increasing agglomeration effect and the subsequent sedimentation of the particle in the electrodeposits layer as the concentration of the additives increase [11]. The image (d) which depicts the structure of the coating of composition Zn-6MgO-18MnO_2 shows rather larger crystal particle size with some defects. The image shows some non-uniform distribution of the plating metal particles with 18g/L concentration of the MnO_2. The strong blocking influence of the induced composite leading to good precipitation and structural change are not directly as a result of the amounts of particle incorporation but upon the additional process parameter especially the plating applied current density.

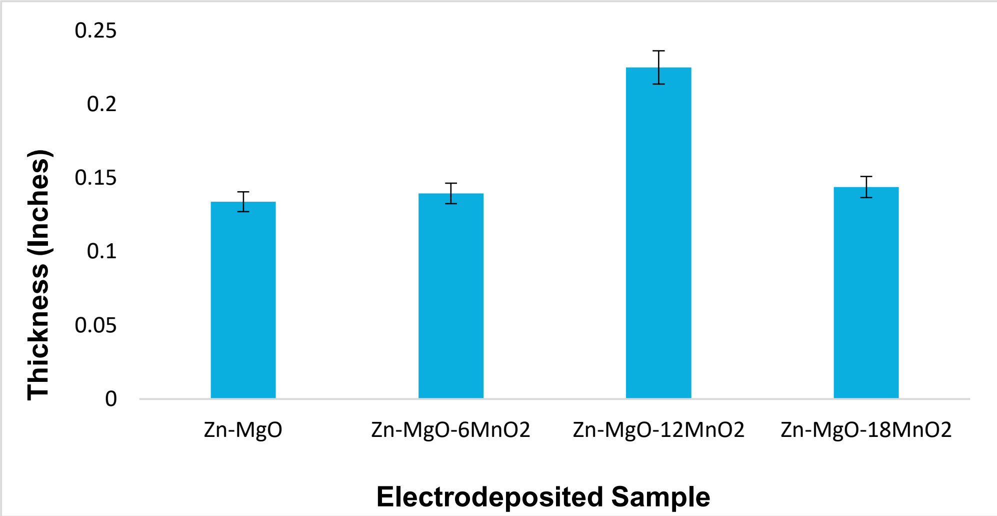

Figure 1: Coating thickness of Zn-MgO/MnO_2 coatings

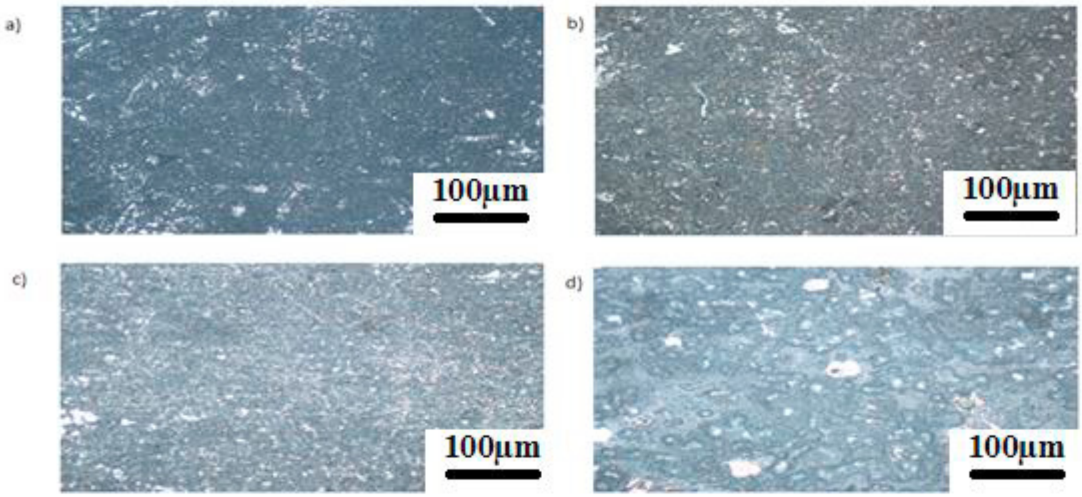

Figure 2: OPM of plated samples, a) Zn-MgO, b) Zn-MgO-6MnO_2, c) Zn-MgO-12MnO_2 and d) Zn-MgO-18MnO_2

The SEM images and EDS of Zn-MgO-12MnO_2 shows the composition of the coating with Zn being the most dominant element on the coating represented by the highest peak. The other smaller peaks represents some of the elements like Ca, Fe, and Mn that already existed in the mild steel before plating. In general, the SEM image displays deposition appearance that exhibits showing plating and good adhesion. There is clumped distribution of the deposits that is visible on the micrograph of this coating that can be due to electrodeposition parameters. The better adhesion that occurs within the interface is a result of the presence of boric acid.

The SEM and EDs above shows the analysis of the coating of sample 4 (Zn-MgO-18MnO_2). The micrograph shows a coating with non-uniform crystal size, with the whole substrate being covered with the metal deposit. The thickness results of the coatings shows that the sample 4 coating is comparably thicker than that of sample 1 and sample 2. According to Popoola, [12] the roughness of the coating increases with the thickness, hence sample 4 is characterized by a rough coating. It is known that the surface roughness of the developed coatings is manly affected by the applied voltage during electrodeposition. The adhesion properties of the fabricated coatings increases due to the applied voltage which is attributed to the fact that film thicknesses are mostly affected by particle size of the materials used, the distance between anode and cathode as well as the depth of immersion [12]. The substrate is well covered with the coating due to the optimum voltage of 2.5 used.

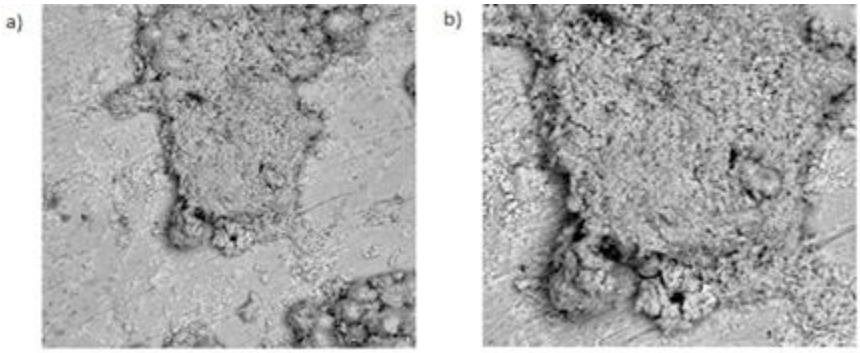

Figure 3: SEM/EDX image of Zn-Mgo-12MnO$_2$ at different magnification

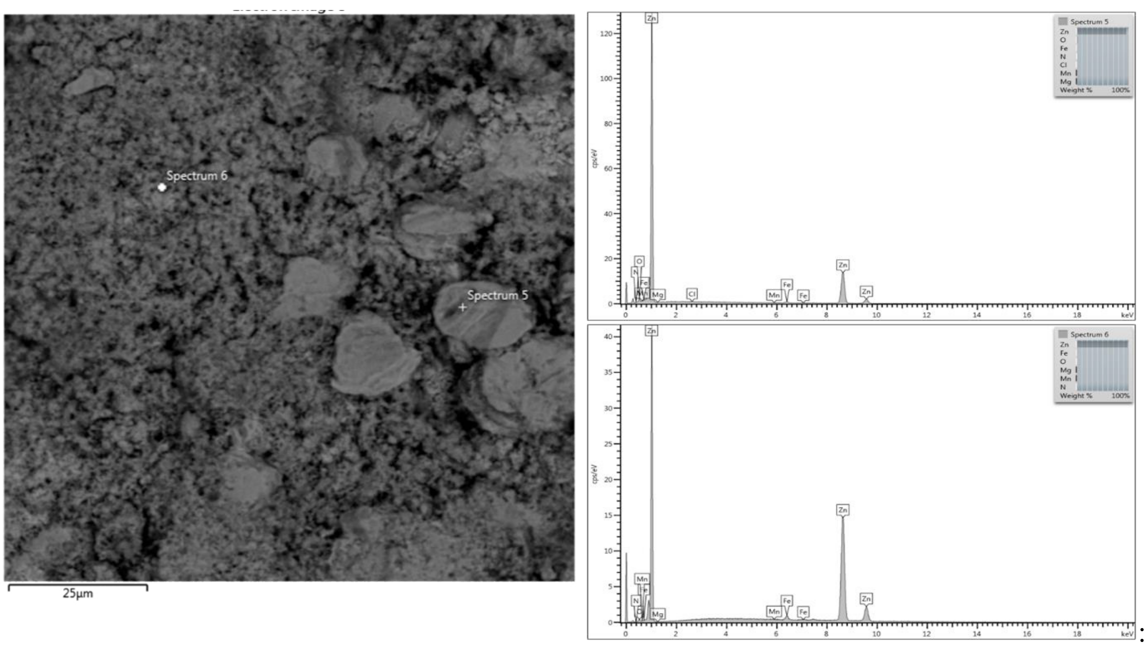

Figure 4: SEM of Sample 3 (Zn-MgO-18MnO$_2$)

3.3 Microhardness properties of the deposited coatings

The figure 5 shows a general increase in the microhardness of the samples as the additives are introduced into the bath and also as the concentration of MnO$_2$ increases. There is a considerable improvement of the hardness of the substrate with the minimum of 82HV and maximum of 96HV, when being compared to the uncoated sample with a value of 58HV.Therefore the study testifies that MnO$_2$ increases the hardness of mild steel as it acts as a reinforcement additive. The significant increase of the hardness can be due to the construction of bond properties of Zn, MgO and MnO$_2$. The OPM of the coatings show a great deal of smoothness in the coatings hence the increased hardness. It has been confirmed that higher microhardness properties of the synthesized coatings as compared to pure mild steel could be attributed to the refinement of grain structure of the deposit. [12].

From this study, the heat treated samples generally have a lower microhardness values than the respective untreated samples (Figure 5). This can be due to the fact that there is an increase in the inter-particle spaces within the precipitate as a result of heat treatment which makes dislocation bowing much easier [13]. Although the samples have a slightly lower hardness than the respective samples, the treated samples still have a significantly improved hardness in comparison to the control.

After heat treatment, the composite coatings were analysed by an optical microscope to give micrographs shown by figure 6. There was no much change in the appearance of sample 1 coating comparing before and after heat treatment micrographs. There was dissolution of coatings on the other samples to which MnO_2 was added. Precipitation of new phases formed can be visibly seen in the respective micrographs above. The precipitations are non-uniform with the coating that have more amount of MnO_2 having the most non-uniform precipitates, thus the sample exhibited much difference in hardness to its untreated sample [13].

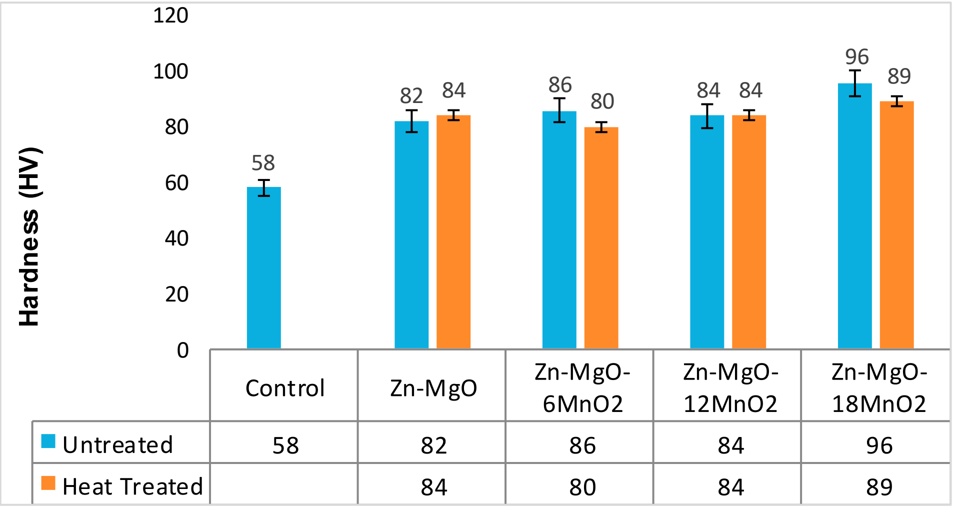

Figure 5: Microhardness analysis of electrodeposited samples and heat-treated samples.

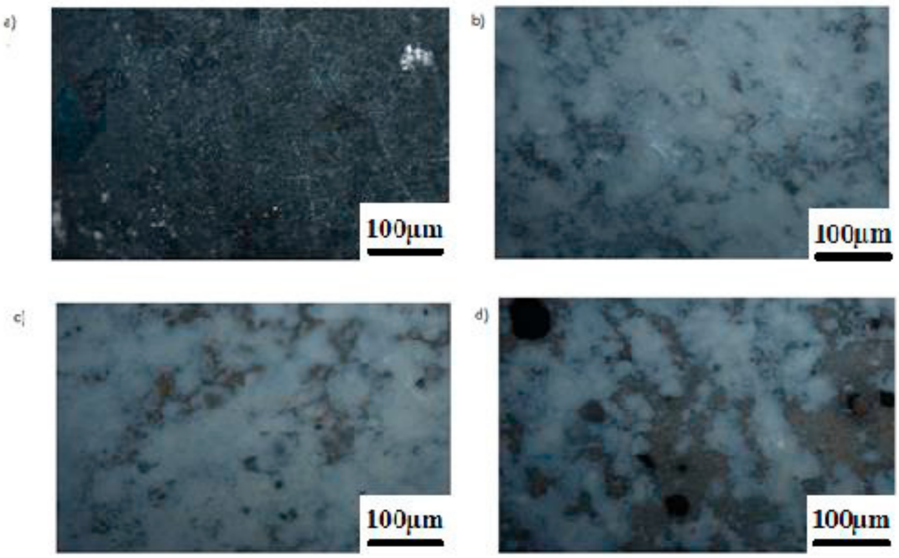

Figure 6: Microstructure of the heat treated (350 °C) composite coatings on mild steel a) Zn-MgO b) Zn-MgO-6MnO_2 c) Zn-MgO-12MnO_2 d) Zn-MgO-18MnO_2

4. Conclusions

Zn-MgO/MnO2 coatings were successfully electrodeposited on low carbon steel. Addition of MnO_2 to Zn-MgO resulted in enhanced microhardness properties. A small decrease in microhardness is discovered after thermal stability of the coatings at 350ºC. Compact optical microscope was revealed after heat-treatment as compact to untreated micrographs.

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References

[1] O. S. I. Fayomi and A. P. I. Popoola, Anti-corrosion properties and structural characteristics of fabricated ternary coatings, *Surf. Eng. Appl. Electrochem.*, pp. 76–84, 2015.

[2] A. C. Hegde, K. Venkatakrishna, and N. Eliaz, "Electrodeposition of Zn-Ni, Zn-Fe and Zn-Ni-Fe alloys," *Surf. Coatings Technol.*, vol. 205, no. 7, pp. 2031–2041, 2010.

[3] B. M. Praveen, T. V. Venkatesha, Y. A. Naik, and K. Prashantha, "Corrosion Behavior of Zn-TiO2 Composite Coating," *Synth. React. Inorganic, Met. Nano-Metal Chem.*, vol. 37, no. 6, pp. 461–465, 2007.

[4] O. S. Fayomi, C. A. Loto, and A. P. I. Popoola, "CORROSION STUDY AND SURFACE CHARACTERIZATION OF ZINC (Zn) AND ZINC-ALUMINIUM (Zn-Al) DEPOSITIONS ON MILD STEEL IN SALINE ENVIRONMENT," *Tshwane Univ. Technol.*, vol. 1, no. May, pp. 1–209, 2012.

[5] S. Ranganatha, T. V. Venkatesha, K. Vathsala, and M. K. P. kumar, "Electrochemical studies on Zn/nano-CeO2electrodeposited composite coatings," *Surf. Coatings Technol.*, vol. 208, pp. 64–72, 2012.

[6] H. Y. Zheng and M. Z. An, "Electrodeposition of Zn-Ni-Al2O3 nanocomposite coatings under ultrasound conditions," *J. Alloys Compd.*, vol. 459, no. 1–2, pp. 548–552, 2008.

[7] W. Tian, F. Q. Xie, X. Q. Wu, and Z. Z. Yang, "Study on corrosion resistance of electroplating zinc-nickel alloy coatings," *Surf. Interface Anal.*, vol. 41, no. 3, pp. 251–254, 2009.

[8] Y. Arthoba NAIK, T. Venkatarangaiah VENKATESHA, and P. Vasudeva NAYAK, "Electrodeposition of Zinc from Chloride Solution," *Turk J Chem*, vol. 26, pp. 725–733, 2002.

[9] O. S. I. Fayomi, A. P. I. Popoola, and V. S. Aigbodion, "Effect of thermal treatment on the interfacial reaction, microstructural and mechanical properties of Zn-Al-SnO2/TiO2 functional coating alloys," *J. Alloys Compd.*, vol. 617, pp. 455–463, 2014.

[10] A. P. Abbott, A. Ballantyne, R. C. Harris, J. A. Juma, and K. S. Ryder, "A Comparative Study of Nickel Electrodeposition Using Deep Eutectic Solvents and Aqueous Solutions," *Electrochim. Acta*, vol. 176, pp. 718–726, 2015.

[11] D. Blejan and L. M. Muresan, "Corrosion behavior of Zn-Ni-Al2O3 nanocomposite coatings obtained by electrodeposition from alkaline electrolytes," *Mater. Corros.*, vol. 64, no. 5, pp. 433–438, 2013.

[12] A. P. I. Popoola, O. S. I. Fayomi, and O. M. Popoola, "Electrochemical and Mechanical Properties of Mild Steel," *Int. J. Electrochem. Sci.*, vol. 7, no. February, pp. 4898–4917, 2012.

[13] M. Abdulwahab, I. A. Madugu, F. Asuke, O. S. I. Fayomi, and F. A. Ayeni, "Effect of thermal ageing treatment on the mechanical properties of antimony-modified A356.0-type Al-Si-Mg alloy," *J. Mater. Environ. Sci.*, vol. 4, no. 1, pp. 87–92, 2013.