Development of an *In-Situ* Composite Doped Coating for Corrosion Protection and Mechanical Properties Enhancements in Process Engineering

Oluwasegun T. Joshua[1], Ojo S. I. Fayomi[2*], Enejoh T. Omeje[3]

[1]Department of Metallurgical & Materials Engineering, Kogi State Polytechnic, Lokoja, Nigeria
[2]Department of Mechanical Engineering, Covenant University, Ota, Nigeria
[3]Department of Mineral Resource Engineering, Kogi State Polytechnic, Lokoja, Nigeria
Email: *Ojosundayfayomi3@gmail.com, *segetin80@yahoo.com

Abstract

Process engineering has been seen as one of the vital tools for improving surface coating phenomena for advance application. In an attempt to improve the mechanical, physical and chemical performance of the steel structure for extended application, $Zn\text{-}CeO_2/ZnCeO_2\text{-}Al_2SiO_5$ thin film composite was fabricated on mild steel using direct electrolytic route. Process variation of Al_2SiO_5 particulate ranges from 5 to 15 g per litre. The embedded coating was characterized using Scanning electron microscope (SEM). The chemical effect of the developed alloy was characterized through linear potentiodynamic polarization experiment and the performances of samples were examined in simulated 3.5% sodium chloride. The microhardness verification study proves that there is significant improvement in hardness trend. The tribological assessment indicated that there is less plastic deformation as a result of the counter body. In all, $Zn\text{-}CeO_2/Zn\text{-}CeO_2\text{-}Al_2SiO_5$ exhibits good stability, with agglomeration and great built up of crystal at the interface.

Keywords

Coating, Mild Steel, Corrosion, Hardness

1. Introduction

Corrosion is an unwanted phenomenon that destroys the lustre and aesthetics of objects and drastically decreases their lifespan. Corrosion is destructive and detrimental to structural, equipment and component failure [1]. The unrelenting

effects of corrosion attack have become a global topic for consideration. Corrosion effect is undesirable causing physical and chemical changes in the property of steel it has attacked [2]. The result of studies in a number of countries in relation to corrosion has attempted to determine the national cost of corrosion. The most comprehensive of these studies was carried out in the United States in 1976 and determined that the total yearly cost of metallic corrosion on the economy was estimated high. Corrosion is still a major problem and slows down the advancement and application of such alloys due to failures which reduce the useful life of the prosthetic and cause more harm in the human body [3] [4].

Electrochemical corrosion occurs when a metal atom changes to a metal ion by the loss of electrons. This is because of the presence of cathodic and anodic areas on a metal surface which reacts with air and moisture in the surroundings. The heterogeneous and impure nature of metals contributes largely to their poor corrosion resistance [5] [6]. Corrosion can be controlled through a range of methods which have varying degrees of success. The methods include the use of inhibitors, coating, protective treatments and the utilization of better designs for structures and equipment, understanding the mechanisms of various forms of corrosion and using materials with high corrosion resistance [7]. This present research examined the performance of mild steel coated $Zn\text{-}CeO_2/Zn\text{-}CeO_2\text{-}Al_2SiO_5$ in a simulated sodium chloride environment. The morphologies of the test samples were studied using SEM while the hardness and wear test was carried out using the Brinell hardness tester and reciprocating wear testing machine.

2. Experimental Procedure

2.1. Preparation of Substrate

The composition of mild steel used in this study is shown in Table 1. Mild steel of dimension (30 mm × 20 mm × 2 mm) and zinc sheets of (50 mm × 20 mm × 5 mm) were prepared. The zinc is commercially available pure zinc (99.99%). Mild steel was polished with different grades of emery papers.

2.2. Bath Formulation

The prepared bath composition with optimized mass concentration is shown in Table 2. The essence of this was to create novel composite plating on mild steel using composite particulates of zinc, aluminium silicate (Al_2SiO_5), cerium (iv) oxide (CeO_2) in varying proportions with the aim of determining the most effective coating.

2.3. Deposition of $Zn\text{-}CeO_2/Zn\text{-}CeO_2\text{-}Al_2SiO_5$

For the pre-plating process, the surface of the samples was prepared using

Table 1. Chemical composition of mild steel sample (%wt).

Elements	C	Mn	Si	P	Al	S	Ni	Fe
Wt%	0.15	0.45	0.18	0.01	0.005	0.031	0.008	Balance

Table 2. Bath concentration and formulation.

COMPOSITION	MASS CONCENTRATION
Zinc Chloride	70 g/L
Cerium (iv) oxide	10 g/L
Boric Acid	5
Glycerin	5 g/L
Aluminum silicate	0 - 15 g
pH	4.5
Temp.	50˚C
Time	10 mins
Current Intensity	1.5 A/cm^2
Thiourea	5 g/L
Sodium Sulphate	5 g/L
Potassium Sulphate	5 g/L

different grades of emery paper in order of 60 μm, 120 μm, 360 μm, 400 μm and 1600 μm grades. Water was used as coolant to avoid burning out of the samples. The pickling of the samples was done in diluted 10% HCl acid solution; this was to remove all organic contaminants and oxides. In the plating process, the metal substrate was immersed in a solution containing the dissolved powders of the metals to be deposited. The working substrate (mild steel cathode) was connected to the negative terminal of the rectifier. The zinc anode was also immersed and connected to the positive terminal of the rectifier as shown in **Figure 1**. The pH used was 4.5, other plating parameters such as current density; voltage and time were kept at 1.5 A/cm^2, 2.0 V and 10 minutes respectively as indicated in **Table 3**. The coatings of the samples were carried out in accordance to ASTM A53/A53M and A153 [8]. Finally, the plated samples were rinsed in distilled water to wash off the salt solution immediately after the electroplating process then air dried. Thereafter, series of characterizations such as the study of morphology via SEM, electrochemical using potentiodynamic polarization experiment, Brinell hardness and wear tester were employed to study the performance of the deposited coatings on the substrate.

3. Results and Discussion

3.1. SEM of Deposited Composite Coating

The SEM structure of Zn-10CeO$_2$, Zn-10CeO$_2$-5Al$_2$SiO$_5$, Zn-10CeO$_2$-10Al$_2$SiO$_5$ and Zn-10CeO$_2$-15Al$_2$SiO$_5$ coated mild steel is shown in **Figures 2-5** respectively. The figures show visible crystallites and homogenously distributed of the particles on the steel. **Figure 4** shows visible integration crystallite of CeO$_2$ nanoparticulates. **Figures 3-5** unveiled to phase due to the integration of CeO$_2$ and Al$_2$SiO$_5$ in the zinc interface which increases as the mass concentration of
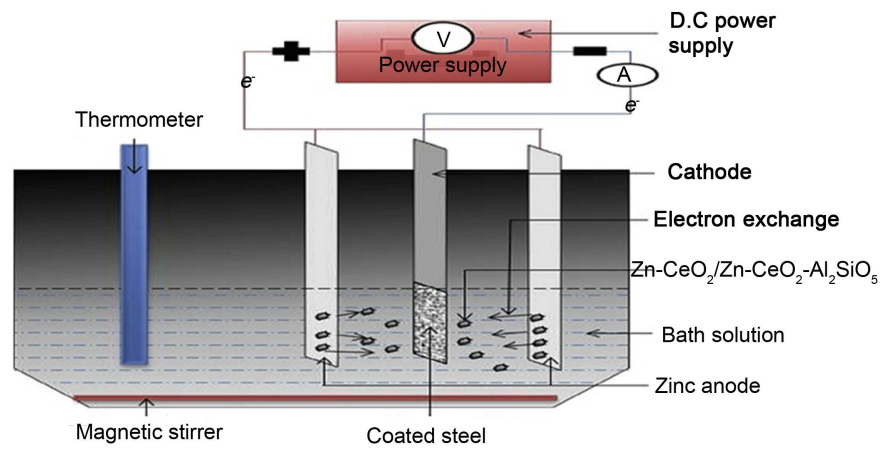
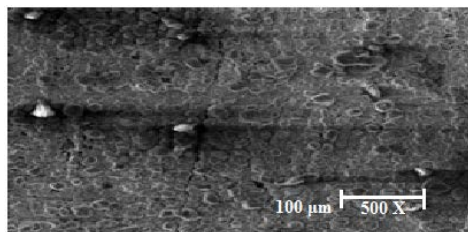**Figure 1.** Schematic diagram of a co-deposition system.
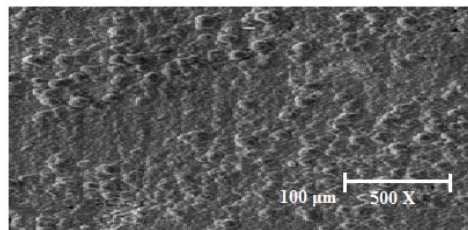

Figure 2. SEM structure of Zn-10CeO$_2$ coated steel.
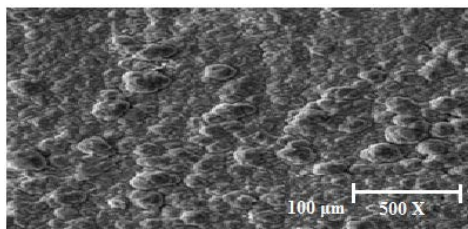

Figure 3. SEM structure of Zn-10CeO$_2$-5Al$_2$SiO$_5$ coated steel.

Figure 4. SEM structure of Zn-10CeO$_2$-10Al$_2$SiO$_5$ coated steel.
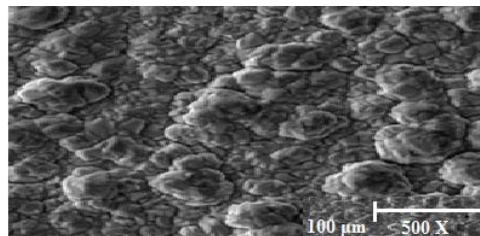
Figure 5. SEM structure of Zn-10CeO$_2$-15Al$_2$SiO$_5$. coated steel.

Table 3. Electrodeposition parameters of $Zn-CeO_2/Zn-CeO_2-Al_2SiO_5$ mild steel.

Sample	Time (min)	Voltage	pH	Current Density (A/cm^2)
$Zn-10CeO_2$	10	2	4.5	1.5
$Zn-10CeO_2-5Al_2SiO_5$	10	2	4.5	1.5
$Zn-10CeO_2-10Al_2SiO_5$	10	2	4.5	1.5
$Zn-10CeO_2-15Al_2SiO_5$	10	2	4.5	1.5

Al_2SiO_5 increases. The synergistic and complementary effect of CeO_2 and Al_2SiO_5 on the coating surface and the interface is responsible for the refined morphology of the coated samples due to the load carrying ability of zinc metal which acts as the nucleation domains and therefore enhancing the formation of the nanocomposites [9] [10] [11] [12].

More so, the slight change in the structure of **Figures 3-5** compared to **Figure 2** could be as a result of Al_2SiO_5 inclusion in the matrix of the nanocomposite which results in the precipitation and enhanced reinforcement [13]. One can therefore conclude that the porosity of the composite coatings reduces with the incorporation of Al_2SiO_5 particles in the coating. This is in accordance to the finding of other authors [11] [14].

3.2. Electrochemical Test Result

The values of corrosion current density (Icorr), corrosion potential (Ecorr), corrosion rate (CR) and polarization resistance (R_p) of the coated and uncoated samples in 3.5% NaCl were obtained from the extrapolation of Tafel plot shown in **Figure 6**. The results reveal the corrosion resisting characteristics of the particles in the test solution. $Zn-CeO_2/Zn-CeO_2-Al_2SiO_5$ was able to block the active sites of the metals from corroding [15] [16]. Corrosion rate of $Zn-10CeO_2-5Al_2SiO_5$ coated sample was the lowest when compared with others as indicated in **Table 4**. This could traceable to the nature and tenacity of the passive film produced by $Zn-10CeO_2-5Al_2SiO_5$ on the surface of the coated steel or chemical stability of the samples [17].

3.3. Microhardness Behaviour of Zn-CeO₂/Zn-CeO₂-Al₂SiO₅ Deposition

Figure 7 shows the mircohardness of the test samples. $Zn-10CeO_2-10Al_2SiO$ coated steel has the highest Brinell hardness value of 203 BHN for the electrodeposited sample. Generally, the coated samples exhibit higher value of hardness compared to the uncoated sample which could be attributed to the strain energy between the particles and the steel [18] [19] (**Table 5**).

3.4. Wear Behaviour of Zn-CeO₂/Zn-CeO₂-Al₂SiO₅ Deposition

The wear behaviour of the uncoated and coated samples is shown in **Figure 8**. The uncoated sample exhibits the highest value of wear loss compared to the coated samples. The uncoated sample has a wear loss of 0.019 g/min while the
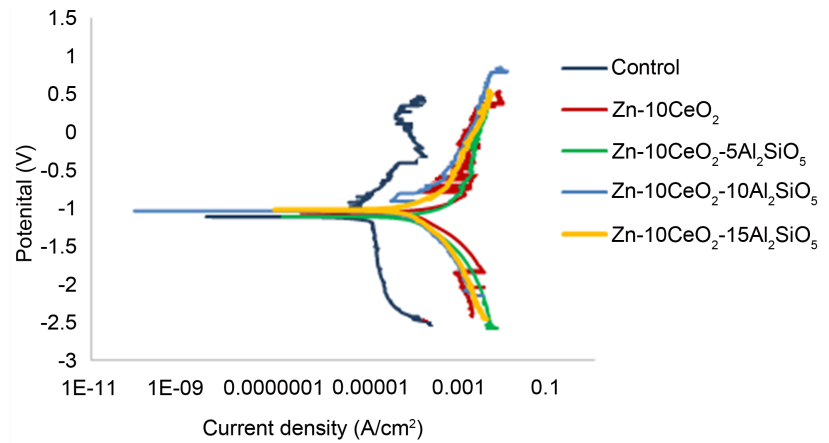
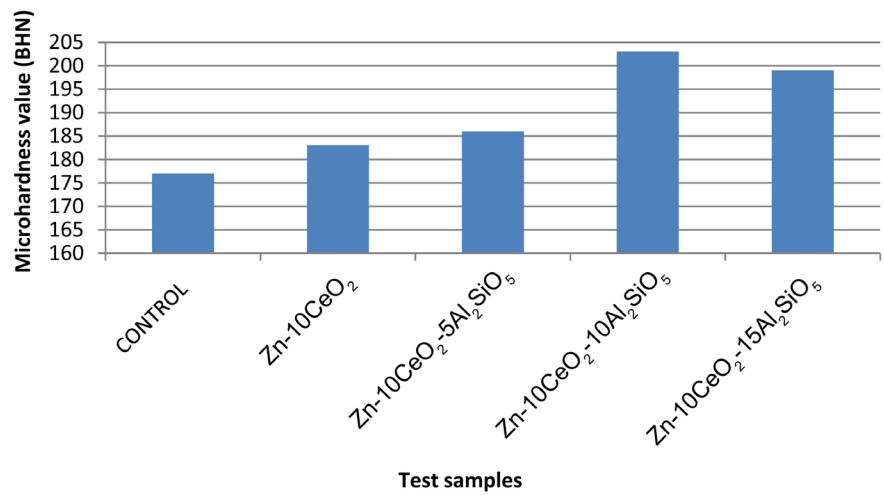**Figure 6.** Potentiodynamic polarization Curves of Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ coated and uncoated samples.

Figure 7. Brinell hardness value for Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ deposition.
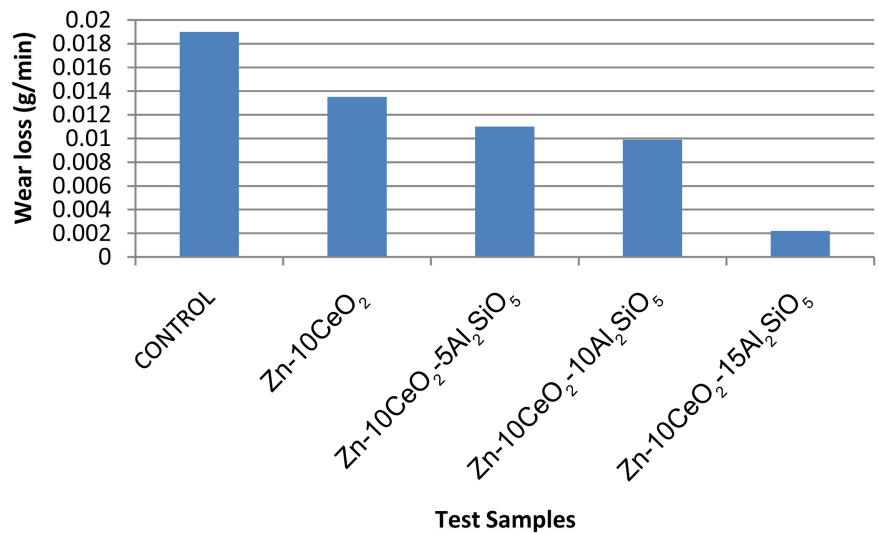
Figure 8. Wear behaviour of Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ deposition.

Zn-10CeO$_2$-15Al$_2$SiO$_5$ coated sample has the lowest wear loss vale of 0.001 g/min. This could be attributed to coherence interaction between the steel and the coating and the processing parameters [18] [20] [21]. The Zn-10CeO$_2$-10Al$_2$SiO$_5$ and Zn-10CeO$_2$-15Al$_2$SiO$_5$ displays lower wear loss which justifies the higher hardness values they possess. This also indicates these samples possess higher strain energy that exists between the coating and the metal interface (Table 6).

4. Conclusion

The inclusion of the CeO$_2$/Al$_2$SiO$_5$ particles in the zinc matrix improved the structural properties and proper dispersion of the particles. The electrochemical result showed that Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ nano composite exhibited good corrosion resistance in 3.5% NaCl. The coated samples were also found to exhibit better microhardness and wear properties compared to the uncoated samples which are an indication that the steels mechanical characteristics have been influenced.

Table 4. Potentiodynamic polarization data of Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ coated and uncoated samples.

Sample	Icorr (A/cm^2)	R$_P$ (Ω)	Ecorr (V)	Corrosion rate (mm/yr)
Control	2.04E−4	198	−1.2122	2.57
Zn-10CeO$_2$	3.38E−07	3184	−1.0942	0.0254
Zn-10CeO$_2$-5Al$_2$SiO$_5$	1.47E−07	4050	−1.0660	0.0171
Zn-10CeO$_2$-10Al$_2$SiO$_5$	3.853E−06	1890	−1.0969	0.0445
Zn-10CeO$_2$-15Al$_2$SiO5	2.19E−06	2197	−1.1086	0.0439

Table 5. Microhardness behaviour of Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ coated and uncoated samples.

Test Samples	Microhardness values (BHN)
Control	177
Zn-10CeO$_2$	183
Zn-10CeO$_2$-5Al$_2$SiO$_5$	186
Zn-10CeO$_2$-10Al$_2$SiO$_5$	203
Zn-10CeO$_2$-15Al$_2$SiO5	199

Table 6. Wear loss behavior of Zn-CeO$_2$/Zn-CeO$_2$-Al$_2$SiO$_5$ coated and uncoated samples.

Test Samples	Wear loss (g/min)
Control	0.019
Zn-10CeO$_2$	0.0135
Zn-10CeO$_2$-5Al$_2$SiO$_5$	0.011
Zn-10CeO$_2$-10Al$_2$SiO$_5$	0.0099
Zn-10CeO$_2$-15Al$_2$SiO5	0.0022

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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