Effect of composite particulate reinforcement on the morphology, anti-corrosion and hardness properties of fabricated Zn-ZnO coatings

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Abstract
Co-deposition of zinc metal matrix with ZnO composite was fabricated from electrolytic chloride based coating consisting of 20-40g/L ZnO particle. The resulting composite coatings were characterized using high optic microscope (OPM). The corrosion resistance properties of Zn-ZnO composite coatings were measure using linear polarization in 3.5% NaCl solution. The variation of amount of ZnO %wt. inclusion of the composite on micro-hardness was investigated using dura scan diamond base micro-hardness tester. The results obtained indicate that the introduction of ZnO particles in the deposition bath obviously increase significantly the hardness properties. The increases in hardness value are attributed to the realization of coherent and even precipitate into the metal lattice. The corrosion polarization resistance also improved slightly as against the MS. It was found that addition of ZnO %wt support strengthening characteristics toward hardness improvement with slight enhancement in anti-corrosion properties.

Keywords: Morphology, micro-hardness, composite, anti-corrosion, coating efficiency

1. Introduction
In the past years, the major advancement in electro-deposition has been tremendous. Electrodeposited zinc coatings are used extensively as a functional and reliable coating because of excellent corrosion resistance, ductility and good hardness with wear resistance. Meanwhile, various factors have been attested to cause challenges in the extensive durability and low life-span of the coating produced by zinc deposition [1-7]. The electro-oxidation behavior aggravate easily at high pH containing environment, in an attempt to controlling electroplating variables to increase hardness and wear resistance, undesired residual stress occurs leading to mechanical failure [5-9].

Since the properties of deposited layers are significant and dependent upon the microstructure, there have been studies on control of structural properties by addressing the choice of plating condition, additive incorporation to provide good bath chemistry and appropriate current type. Particles especially inert oxide when introduced into metal matrix changes the functional properties from different literature studied [5-8]. It is also known fact that ceramics composite of a metallic such as Al2O3, ZrO2, TiO2 and SiO2 containing a dispersion of secondary phase gives a novel characteristics such as a good hardness and corrosion resistance [9-10].

Furthermore, it was reported by [10-13] that the amount of composite incorporation in the metal lattice has effect on the crystal growth and the morphological properties. Although, the promising results in understanding the behavior of ZnO in Zn-rich have been reported in few literature however our aim in this work is to examined
the influence of particle loading, current density on the behavioral properties of Zn-ZnO fabricated coating on their microstructure and mechanical properties.

2. Experimental Procedure:

The formulated deposited bath is composed of 150 g L\(^{-1}\) ZnCl, 70gL\(^{-1}\) KCl, 20-40gL\(^{-1}\) ZnO, 10gL\(^{-1}\) H\(_2\)BO\(_3\), 5 g L\(^{-1}\) glycine, and 5 g L\(^{-1}\) thiourea. Analytical reagents and deionized water were used to prepare the plating solution. The deposition setup tests were conducted on a set up vessel connected to a laboratory rectifier. The bath was stirred by a magnetic stirrer consistently with about 100 rpm at 40°C. The experiments were conducted at current density between 0.5-1 A/cm\(^2\), and applied potential of 0.3-0.6V. A carbon steel sheet of 20mm×40mm by 2mm was used as the cathode and zinc plate of a size of 25mm×50mm by 3mm with a well prepared surface was used as the anode. The spectrometer chemical composition of the substrate is described in table 1 and the varied deposited parameter are illustrated in table 2

![Table 1: Chemical composition of mild steel used (wt%)](image1)

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Ni</th>
<th>Fe</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0.15</td>
<td>0.45</td>
<td>0.18</td>
<td>0.01</td>
<td>0.031</td>
<td>0.005</td>
<td>0.008</td>
<td>Balance</td>
<td></td>
</tr>
</tbody>
</table>

![Table 2: Experimental study parameter of Zn-ZnO ceramic composite deposition](image2)

<table>
<thead>
<tr>
<th>Sample Order</th>
<th>Material sample</th>
<th>Time of deposition (min)</th>
<th>Potential (V)</th>
<th>Current (A/cm(^2))</th>
<th>Con. of additive (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sample 1-A1</td>
<td>Zn-20-ZnO</td>
<td>15</td>
<td>0.3</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Sample 2-A2</td>
<td>Zn-20ZnO</td>
<td>15</td>
<td>0.6</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>Sample 3-A3</td>
<td>Zn-40ZnO</td>
<td>15</td>
<td>0.3</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>Sample 4-A4</td>
<td>Zn-40ZnO</td>
<td>15</td>
<td>0.6</td>
<td>1.0</td>
<td>40</td>
</tr>
</tbody>
</table>

Prior to that the working substrates were sequentially cleaned in ethanol and distilled water for 10 min, rinsed with 5% H\(_2\)SO\(_4\), washed in distilled water, and then deep instantaneously in the bath formulated to allow the deposition of the target ceramic composite coatings. The deposited sample after plating was sectioned into appropriate dimension and make ready for characterization. The morphologies of the composite coatings were observed with the help of high magnification optical microscope. The hardness of the composite coatings was measured with high diamond Vickers’ microhardness tester. The electrochemical studies were performed with Autolab PGSTAT 101 Metrohm potentiostat using a three-electrode cell assembly in a 3.65% NaCl static solution at 40°C. The developed composite was the working electrode, platinum electrode was used as counter electrode and Ag/AgCl was used as reference electrode. 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 linear polarization resistance was obtained.

1.0. Result and Discussions:

1.1. Morphological studies:

Figure 1-4 shows the micrographic structure of represented Zn incorporated ZnO fabricated ceramic coating at different concentration of particle and applied current density. In general all the deposited Zn-ZnO coatings at different matrixes show a homogeneous and defect free at the interface. The additive with smaller particle introduction at 0.5A/cm\(^2\) into the zinc electrolyte shows better coating adhesions which hence provide uniform distribution of the particulates. It has been reported [9-10] that a particle incorporation characteristic on the electrodeposited layer is a function of current density. At 40g/L of embedded ceramics composite in 0.5A/cm\(^2\) larger hexagonal crystallite were seen. It is obvious that the controlled of adsorption of the particles could only be efficient with the control of the doped ceramics in the metal blend in relation to the rate of applied current density [8,10]. In 40g/l, 0.5A/cm\(^2\) (Figure 3) system concentration accelerates both the agglomeration effect and the subsequent sedimentation of the particle in the electrodeposits layers. The stability is quite evident with better interlocking of the matrix at interface compared to the fabricated coating at 1.0A/cm\(^2\) which shows non-
uniform distribution and such deposits could upset the foreseen performance since rate of deposition is faster as a result of increasing current density (see Figure 4).

![Figure 1: Morphology of Zn-20ZnO -0.5A composite coating](image1)

![Figure 2: Morphology of Zn-20ZnO-1.0A composite coating](image2)

Furthermore, the deposition appearance with coating interferes of ZnO was quite appreciated in that particulate strengthen composite find its way expressly doped into the zinc metal matrix. Fig. 4 also signifies that the crystallites size of zinc decreases in the presence of the ZnO particles. Hence it is important to mention that the co-deposition process is a function of competitive ions of Zn^{2+} and the particle of the active site which is in line with the observation by [7] on composite incorporation. In all, zinc metal as load bearer, the dispersion of the particulate cover the nucleation site and strengthening the produced coatings. In other words, it is necessary to mention that 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 3: Morphology of Zn-40ZnO-0.5A composite coating](image3)

![Figure 4: Morphology of Zn-40ZnO-1.0 A composite coating](image4)
1.2. Micro-hardness studies
The micro-hardness (HVN) value of the deposited coatings at each deposition matrix is presented in Fig. 5 at different current density. From all indications, hardness increased from 33.4 HVN to approximately 136 HVN which was measured along the surface of the coating mild steel substrate. The observed improvement in micro-hardness of deposited sample was observed to double the micro-hardness of substrate especially with Zn-20ZnO at 0.5A/cm². This progression was attributed to the formation of adherence intermetallic phase and the conditioning effect of ZnO ceramics in the zinc metal electrolyte. Although, all ceramics composites coating produced gave a good micro-hardness behavior, it is noteworthy to mention that strengthening behavior in relation to the improved micro-hardness trend is function of robust microstructure [4-7]. The trend of improvement of the micro-hardness is traced from different weight fraction hardening particle incorporation, atomic bonding system and applied current densities. For deposits produced at 0.5A/cm² significant improvement was observed than other coating produce at 1.0A/cm². This implies that at faster deposition rate, necessary ions and particle deposits at the cathode are irregularly deposited leading to larger grain and poor structural characteristics. In line with this believe, at low current density the migration of the particle converse preferred surface modification and fine grains. This obviously obstructs the easy movement of dislocations, to give a higher hardness value of deposited samples for all fabricated coatings at 0.5A/cm².

![Figure 5: Hardness trend of the Zn-ZnO composite coating matrixes](image)

1.3. Anti-corrosion properties
Figure 6, Table 3 shows the linear polarization Tafel plots acquired test of the deposited alloy in 3.65 % NaCl solution. The anodic and cathodic site Tafel value and corrosion current density derived after extrapolations are given in details as observed in Table 3. The corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$) and corrosion rates (CR) were obtained from the tafel plots and are recorded. As can be seen, composite coating fabricated does not give a significant and excellent corrosion resistance with lower corrosion potentials and corrosion current densities change as against the control mild steel sample. The little positive shift in corrosion potential to -1.3516 (mV) for Zn-20ZnO alloy at 0.5A/cm² indicates fear corrosion resistance than that of the Zn-40ZnO alloy at 0.5A/cm² with -1.3725 (mV). The same trend also goes for the binary coating system of Zn-20ZnO alloy at 1.0A/cm² with corrosion potential of -1.3934 mV against -1.4022mV for Zn-40ZnO alloy at 1.0A/cm². In all cases, the potential of all formulated and fabricated coating matrix yielded little more improved potential than the as-received sample with -1.53900 mv. The corrosion rate and $i_{corr}$ subsequently follows the same trend.
Figure 6: Linear Polarization plot of Zn-ZnO composite coating.

Table 3: Tafel polarization data of Zn-ZnO composite coating at 0.5-1.0A co-deposition matrix

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr, Obs}$ (V)</th>
<th>$j_{corr}$ (A/cm²)</th>
<th>$C_r$ (mm/yr)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1(Zn-20ZnO)0.5A</td>
<td>-1.3516</td>
<td>0.001166</td>
<td>0.96796</td>
<td>291.38</td>
</tr>
<tr>
<td>A2(Zn-20ZnO)1.0A</td>
<td>-1.3934</td>
<td>0.002365</td>
<td>1.7493</td>
<td>28.122</td>
</tr>
<tr>
<td>A3(Zn-40ZnO)0.5A</td>
<td>-1.3725</td>
<td>0.002310</td>
<td>1.6231</td>
<td>80.705</td>
</tr>
<tr>
<td>A4(Zn-40ZnO)1.0A</td>
<td>-1.4022</td>
<td>0.002524</td>
<td>1.8842</td>
<td>10.216</td>
</tr>
<tr>
<td>Control</td>
<td>-1.53900</td>
<td>7.04E-02</td>
<td>4.100000</td>
<td>27.600</td>
</tr>
</tbody>
</table>

Since particle entrapments into the metal lattices take place through the mechanism of adsorption which entails formation of solid precipitation at interface; the particle surface area and good throwing power. From Figure 7, the trend of coating efficiencies was evaluated in relation to the degree of particle migration into the cathode surface. However, from our studies, we foresee that the dissolving capacity is a function of mass of dissolving particle on the base solution and inversely proportion to the surface area, throwing power and time of deposition. Therefore the assumed prediction equation might be

$$V = M \frac{I}{AWT}$$  \hspace{1cm} (1)

Where $V$ is the dissolving capacity, $M$ is the mass of the dissolving particulate, $A$ is the surface area, $W$ is the throwing potential or current density. Hence,

$$V = \frac{KM}{AWT}$$  \hspace{1cm} (2)

With the above relationship a possible corrosion progression was proposed from the polarization data to evaluate the efficiencies of individual coatings. From the comparative examination chats, it was apparent that the coating efficiency from all process agreed to some extend and showed improved properties in all regards especially with the coatings produced at lower particle incorporation. With average of 97% efficiencies, adsorption characteristics and incorporation of the metal lattices can be seen to center around the interfacial effect of the induced particulate [9-10].
Conclusions
1) ZnO have been successfully co-deposited with Zn metal matrix to fabricate Zn-ZnO at various process parameters.
2) Good distribution of the ZnO in the microstructure at different matrix were attained which support the enhancement of the micro-hardness properties of the fabricated coatings.
3) The anti-corrosion resistance property of the coating has a little improvement on the mild steel to some extent. Although, the corrosion resistance increase with the increase in additive concentration.
4) Improved hardness characteristic and coating efficiencies attained are attributed to the particle incorporation on zinc-rich interface.

References

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