1. Introduction

Zinc alloy/nanocomposite coatings have received a great research interest in the past years. This is due to their enhanced performance in harsh environments compared to the traditional Zn coatings. Metals and metal oxides, carbides, nitrides or borides are incorporated into the metal matrix to enhance the quality of the coatings. These nano-materials possess unusual and excellent properties that are not exhibited in the traditional bulk material of the same kind. The properties include good corrosion and wear resistance, biocompatibility, thermal stability and self-lubrication [1]-[3]. Electrodeposition is one of the techniques that is used for incorporation of these particles into a metal matrix. Some advantages electrodeposition has over other deposition techniques include low cost, flexibility and ease of operation, high production rate, easily available equipment and less contamination [4].

Simple oxides such as Al₂O₃, TiO₂, ZrO₂, CeO₂ and SiO₂ are commonly used due to their ease of availability. These oxides can be incorporated into plain Zn matrix or Zn alloy [4]-[10]. Al₂O₃ nanoparticles were found to improve electrochemical behavior of Zn-Ni when they were incorporated within the optimal concentrations. It was established that these particles have significant effect on the surface morphology of the coatings [6]. Reference [7] found that the hardness was also improved due to the incorporation of the particles aided by ultrasound conditions. Research has shown that incorporation of Cr₂O₃ into a metal matrix yields positive results on the mechanical and thermal properties such as microhardness, wear resistance and thermal stability. However, no significant effect was found on the electrochemical behavior of the matrix [11].

There is no sufficient information in the available literature that provides insight about incorporation of Al₂O₃ and Cr₂O₃ nanoparticles into Zn matrix and their special properties. Therefore, this research aims to fabricate Zn-Al₂O₃ and Zn-Cr₂O₃ nanocomposite coatings and compare the properties that can be impacted by these nanoparticles on Zn matrix for advanced industrial applications.

2. Experimental

The study of the thermal, wear and corrosion properties of developed nanocomposite coatings of Zn-Al₂O₃ and Zn-Cr₂O₃ was carried out. The coatings were produced by electrodeposition technique from chloride acidic bath. Laboratory tube furnace was used for the thermal analysis. The wear test was performed using CETR tribo-tester dry reciprocating tester. The hardness properties were investigated using diamond base Dura microhardness tester. Scanning electron microscope (SEM) affixed with energy dispersive spectrometry was used to study the morphological characteristics, before and after wear deformation. The corrosion degradation behavior was observed using linear polarization technique in 3.5% NaCl. In all the interaction, the effects of the incorporated Al₂O₃ and Cr₂O₃ nanoparticles on zinc rich coatings were found to have an excellent influence on the wear, corrosion and thermal stability properties. The fabrication and properties exhibited by the alloys were therefore found to be satisfactory and shows good predictability and applicability.

Keywords: Microstructure, corrosion, nanocomposite coatings, thermal stability, tribology
400 grit SiC emery papers to remove the unwanted material on the substrate. Degreasing followed by suspending the samples into ethanol, dipped into 1M hydrochloric acid to activate the surface and then rinsed in water before plating. Two Zinc (99.9%) plates were used as anodes. The solutions for plating were prepared a day prior to the tests. To ensure even dispersion and prevent agglomeration of the nanoparticles of Al$_2$O$_3$ and Cr$_2$O$_3$ which were added into the bath, the solutions were mechanically stirred for 18hrs using a magnetic stirrer. Sigma Aldrich spherical Al$_2$O$_3$ and frosty like shaped Cr$_2$O$_3$ powders (Fig. 1) with average diameter of 50 and 100 nm respectively were used with no prior treatment from the supplier. Adjustment and keeping the pH at 3.8 was made by addition of hydrochloric acid or sodium hydroxide. All the electroplating tests were conducted under ambient conditions at a plating time of 20 min and of speed of 300 rpm. The plated samples were then rinsed in water for 5 seconds and then left to air dry. The thickness of the produced coatings was measured to be about 25 µm. Vega Tescan scanning electron Microscopes (SEI mode) equipped with Energy Dispersive Spectrometry was used to study the surface morphology and content of the incorporated particles in the deposits.

Potentiodynamic polarization technique was used to investigate the corrosion behavior of the coatings in 3.65% NaCl environment using µAUTOLAB Pontentiotstat/ Galvanostat. The polarization measurements were carried at a scanning rate of 0.01 V/s at a potential range of -1.5 to 1.5V. Corrosion parameters from polarization studies were obtained by extrapolations of the anodic and cathodic Tafel slopes. Saturated calomel electrode was used as a reference and graphite served as a counter electrode. A diamond indenter microhardness tester was used to investigate the microhardness of the deposits. An average of three measurements in different locations of the sample was taken to ensure correct and accurate values that represent the specimen. The samples were exposed to annealing temperature of 250 °C in a laboratory tube furnace. The duration range of the heat treatment was 0.5, 2 and 16 hours to evaluate the thermal stability of the coatings with respect to time. Microhardness evolution of the coatings was followed according to the duration range. CETR tribo-tester was used to study the wear characteristics of the coatings under dry reciprocating conditions. A normal load of 5N and a velocity of 2 m/s at a sliding distance of 2 mm were used as operating variables. The coefficient of friction was continually recorded for 1000s in all the tribology tests. Dry abrasion rig machine was used to determine the percentage wear mass loss under dry sliding conditions using silica sand as a wearing medium at a speed of 200 rev/ min for 60 s. The initial mass of the samples were weighed before the tests and the final masses were recorded after the dry sliding. These values were used to determine the percentage wear mass loss.

<table>
<thead>
<tr>
<th>Sample Codes</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA1</td>
<td>Zn-5g/L Al$_2$O$_3$</td>
</tr>
<tr>
<td>ZA2</td>
<td>Zn-10g/L Al$_2$O$_3$</td>
</tr>
<tr>
<td>ZC1</td>
<td>Zn-10g/L Cr$_2$O$_3$</td>
</tr>
<tr>
<td>ZC2</td>
<td>Zn-20g/L Cr$_2$O$_3$</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Morphological Studies

The surface morphologies of Zn, Zn-Al$_2$O$_3$ and Zn-Cr$_2$O$_3$ nanocomposite coatings are shown in Figure 2. Pure Zn coating shows a flake-like crystalline structure (Fig. 2a) with coarse grains and surface defects (micro holes and pores). These defects can serve as weak sites for the degradation of the quality of the coatings when they are exposed to trying environments. ZA1 (Fig. 2b) and ZC2 (Fig. 2c) follow a similar arrangement but exhibit uniform and compact microstructure with smaller crystal grains. Incorporation of nanoparticles into a metal matrix induces grain refinement by impeding the growth of the crystals. Therefore, the modification of the morphological characteristics of the Zn coatings can be attributed the incorporation of Al$_2$O$_3$ and Cr$_2$O$_3$ nanoparticles into matrix. EDS results as shown in Figure 4 confirmed the presence of Al$_2$O$_3$ (2.2 wt %) and Cr$_2$O$_3$ (7.38 wt %) in the coating. The cross-section micrographs are also presented in Figure 3 and show that the particles are incorporated into the Zn matrix.

Fig. 1. SEM image of received (a) Al$_2$O$_3$ and (b) Cr$_2$O$_3$ powders

Fig. 2. SEM micrographs (a) Zn coating (b) Zn-5g/L Al$_2$O$_3$ coating and (c) Zn-20g/L Cr$_2$O$_3$ coating
Fig. 3. SEM images of the cross section (a) ZA1 and (b) ZC2 nanocomposite coatings

Fig. 4. EDS spectrum for (a) ZA1 and (b) ZC2 nanocomposite coatings

Fig. 5. X-ray diffractograms of (a) Zn coating, (b) ZA1 composite coating and (c) ZC2 composite coating

3.2. Structural and Microhardness Studies

XRD was used to study the effect of the incorporated nanoparticulates on the average crystallite size and crystallographic orientation on Zn matrix. The XRD patterns of Zn, ZA1 and ZC2 coatings obtained are shown in Figure 5. The major diffraction lines can be attributed to Zn hexagonal structure. The composites follows the same pattern but with different peak intensities. The modification in peak intensities indicates the presence of the nanoparticles in the coating. The peak width of the composites was also found to be slightly broader than that of the matrix.

Full width at half maximum (FWHM) of (101) peak was then used to calculate the crystallite sizes of the coatings using Sherrer equation:

\[ D = \frac{K\lambda}{B\cos\theta} \]

Where D is the diameter of the crystal, K the Sherrer factor (=1), \( \lambda \) radiation incident wavelength, B the line width and \( \theta \) is the position for (101) peak.

The reinforcement of the coating with Al\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) particles reduced the average crystallite size of the matrix from 31 to 15 and 28 nm respectively.

The incorporation of nanoparticles increases nucleation sites and thus disturbing crystal growth. Nanoparticles were also reported to adsorb on the growing crystal and impede its further growth resulting in smaller crystal sizes [3, 21].

Figure 6 shows effect of bath particle concentration on the microhardness property of the coatings. It is evident from the figure that all the composite coatings exhibited improved microhardness values as compared to as received and plain Zn samples. Therefore, this result can be attributed to the incorporation of the nanoparticles into the Zn matrix. The presence of these particles in the coating hinders the crystal growth of Zn by increasing the number of nucleation sites and thus reducing the grain size. Several authors have reported similar results when these nanoparticles were incorporated into metal matrices to form a composite alloy [7], [11].

Addition of 5 g/l of Al\(_2\)O\(_3\) nanoparticles into the electrolyte solution yielded maximum microhardness of 192 HV for ZA composite coatings. Further increment of the particles from 5 to 10 g/l had no significant influence in microhardness of the coatings. Loading of particles in the bath beyond optimal concentrations promotes agglomeration and reduce efficiency of uniform codeposition. This leads to generation of defects in the resultant deposits and hence the decrease in microhardness when the particle loading was increased to 10 g/l. On the other hand, increase of Cr\(_2\)O\(_3\) particles from 10 to 20 g/l improved the microhardness from 161 to 228 HV. The improvement in microhardness yield obtained here is in agreement with Gugliemi’s two step absorption model. The model states that increasing bath particle content increases the chance of particles to be codeposited at the cathode [13]. This suggests that coatings fabricated from baths containing high particle concentration contain the highest particle content and hence improved coating quality. Therefore, the 228 HV microhardness yield obtained can be attributed to the increased Cr\(_2\)O\(_3\) particles in ZC2 composite coating.
3.3. Corrosion Studies

The polarization measurements to evaluate the corrosion behavior of the samples were carried out in a 3.65% NaCl environment under ambient conditions in a potential range of -1.5 to 1.5 V. Figure 7 shows the polarization curves of as received, Zn, Zn-Al$_2$O$_3$ and Zn-Cr$_2$O$_3$ nanocomposite coatings. A positive shift in potential can be observed for all the composite coatings when compared to as received sample. However, a different behavior was observed when the composite coatings were compared with Zn matrix. A negative potential shift was obtained for all the composites except for ZA1. Zn possesses good anti-corrosive properties and protect mild steel from corrosion attack when it is used as protective coating. The main constituent of all the composite coatings is also Zn. When 5g/L of Al$_2$O$_3$ was added into the bath to co-deposit on mild steel with Zn, an increase in potential from -1.1282 (Zn) to -1.0562 V (ZA1) was obtained. A substantial decrease in current density from 12.8 to 0.22 µA/cm$^2$ and increase polarization resistance from 0.957 to 4.16 kΩ corresponds with the positive shift in potential. These results can be attributed to the incorporation of Al$_2$O$_3$ nanoparticles into Zn matrix. Incorporation of these particles into the matrix has been reported to exhibit inhibiting effect on metal corrosion and thus enhancing corrosion resistance of the coatings.

The uniform distribution of the nanoparticles in the Zn matrix fills the micro holes, pores and other surface defects that can promote exposure of the matrix to corrosive medium, and reduces the active sites for corrosion attack. However, further increase of the particles from 5 to 10 g/L in the bath yielded no positive results. This may be due to agglomeration of particles in the bath when they are added beyond optimal concentration leading to formation of non-uniform deposits. Blejan et al obtained similar results when Al$_2$O$_3$ particle loading exceeded the optimal concentration [6]. An improvement in corrosion resistance was observed when Cr$_2$O$_3$ nanoparticles concentration was increased from 10 to 20 g/L. A substantial decrease in current density from 47.8 to 10.7 µA/cm$^2$ and increase in polarization resistance from 0.758 to 1.263 kΩ for ZC1 and ZC2 have been observed. However, this result poses no significance when compared with plain Zn. Therefore, ZA1 stands as the better coating compared to all the coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$R_p$ (Ω)</th>
<th>$E_{corr}$ (V)</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>0.002761</td>
<td>55.565</td>
<td>-1.406</td>
<td>2.412</td>
</tr>
<tr>
<td>Zn</td>
<td>1.28E-05</td>
<td>957.57</td>
<td>-1.1282</td>
<td>0.012</td>
</tr>
<tr>
<td>ZA$_1$</td>
<td>2.22E-07</td>
<td>4160.74</td>
<td>-1.0562</td>
<td>0.0002</td>
</tr>
<tr>
<td>ZA$_2$</td>
<td>2.17E-05</td>
<td>846.52</td>
<td>-1.1382</td>
<td>0.017</td>
</tr>
<tr>
<td>ZC$_1$</td>
<td>4.78E-05</td>
<td>758.13</td>
<td>-1.1972</td>
<td>0.0515</td>
</tr>
<tr>
<td>ZC$_2$</td>
<td>1.07E-05</td>
<td>1263.8</td>
<td>-1.1075</td>
<td>0.007</td>
</tr>
</tbody>
</table>

3.4. Thermal Stability

Evaluation of thermal stability of the nanocomposite coatings was conducted by exposing the samples to annealing temperature of 250 °C. Figure 8 shows the thermal behavior of the samples obtained after they were exposed to heat treatment for duration range of 0.5, 2 and 16 hours at 250 °C.

The evaluation of the heat treated samples followed a microhardness evolution to determine their thermal stability. The figure shows a decrease in microhardness of all the samples with respect to time of exposure but the composites maintain higher values than that of Zn. These values are
maintained higher throughout the experiment. From the observed results, it can be deduced that the composites exhibit better thermal stability properties than Zn and this is attributed to the incorporation of the nanoparticles into Zn matrix. The incorporation of these nanoparticles into a metal matrix slows down grain growth and surface oxidation [14]. Notably, Zn-Cr$_2$O$_3$ can be seen to be more stable than Zn-Al$_2$O$_3$ indicating that Cr$_2$O$_3$ nanoparticles exhibit better thermal properties than Al$_2$O$_3$.

3.5. Tribological Behavior

Figure 9 shows the wear performance of as received sample, Zn coating, Zn-Al$_2$O$_3$ and Zn-Cr$_2$O$_3$ nanocomposites which were tested at a constant normal load of 5 N for a maximum duration of 1000 seconds under dry reciprocating sliding conditions.

The average friction coefficient values of the samples are presented in Figure 9(b). The figure reveals a decrease in coefficient of friction for all the coatings. The high coefficient of friction of as received sample (0.13) is reduced to 0.074 when the mild steel was coated with Zn. A further decrease to 0.011 and 0.016 are obtained when Al$_2$O$_3$ and Cr$_2$O$_3$ were incorporated into Zn matrix respectively. These results suggest that the incorporated nanoparticles provide lubricating properties to Zn matrix by reducing direct contact of the tungsten carbide ball with metal matrix. ZA1 nanocomposite coating exhibit the lowest coefficient of friction followed by ZC2. This indicates that Al$_2$O$_3$ particles possess better self-lubricating properties than Cr$_2$O$_3$ when incorporated to Zn matrix. Reduction in coefficient of friction results in lower mass loss due to wear. The results obtained by Lee showed a correlation between friction coefficient and mass loss; these two factors are directly proportional [17].

The wear percentage loss values of as received, Zn, ZA1 and ZC2 are shown in Figure 10. The figure shows that as received sample exhibit high wear loss (0.695 wt%) as compared to the all the coatings. Coating the sample with Zn reduced the wear loss of as received sample to 0.517 wt%. The inclusion of Al$_2$O$_3$ and Cr$_2$O$_3$ nanoparticles into the Zn matrix further reduced the wear loss to 0.136 and 0.393 wt% respectively. These results support the friction tests and prove that the incorporation of these nanoparticles have significant effect on the wear resistance of Zn coatings. The reduction in wear loss due to the incorporation of the nanoparticles can be attributed to the excellent self-lubricating properties exhibited by these nano-materials. A possible formation of a protective barrier between the wear media and the Zn matrix by the particles can also affect the wear behavior of the coatings. Al$_2$O$_3$ nanoparticles incorporation into Zn matrix showed to be the better materials to improve wear resistance as compared to Cr$_2$O$_3$ particles.

The surface morphology of the worn out samples have been investigated to study the nature of wear and the magnitude of damage caused by the wearing wheel. Figure 11 shows the worn surface morphologies of as received sample, plain Zn
6
coating, Zn-Al$_2$O$_3$ and Zn-Cr$_2$O$_3$ nanocomposite coatings. The worn out surface of as received sample exhibit parallel micro-
ploughing, microcracks and grooves as it can be observed in
Figure11 (a). The nature of damage that has been caused on this
sample during the wear tests suggest that the mechanism of wear
associated with scars on the micrographs is mainly abrasive
wear. Zinc coating (Fig. 11b) in the absence of additives shows
a similar behavior as the as received sample but possesses
fewer furrows, microcracks and grooves. The coating is also
peeled from the substrate and the mild steel surface can be
seen. The extents of damage of ordinary zinc as compared to
as received sample suggest that the presence of Zn on the mild
steel substrate reduced the wear mass loss. Partial peeling of
the coating have been observed on the worn out surfaces of
the nanocomposite coatings indicating the interface bonding
strength between the composite and the substrate is stronger
than that of plain Zn. This result also shows that the composite
coatings exhibited better wear resistance as compared to
as received and Zn coating. Therefore, the improved wear
resistance of the composites can be ascribed to the presence of
Al$_2$O$_3$ and Cr$_2$O$_3$ nanoparticles in the Zn matrix. ZA1 (Fig. 11c)
shows less damage than ZC2 (Fig. 11d) and proves that Al$_2$O$_3$
particles have better self-lubricating properties than Cr$_2$O$_3$.

4. Conclusion

Zn-Al$_2$O$_3$ and Zn-Cr$_2$O$_3$ nanocomposite coatings were
successfully fabricated using electrodeposition technique
in chloride bath solution. The effect of the incorporated
nanoparticles on the surface morphology, microhardness,
corrosion resistance, thermal stability and wear properties
were studied and compared. Scanning electron microscope
micrographs showed that both Al$_2$O$_3$ and Cr$_2$O$_3$ have significant
effect on the morphology of the coatings and EDS confirmed
the presence of the nanoparticles. Al$_2$O$_3$ incorporation
improved the corrosion resistance while Cr$_2$O$_3$ had no
significant effect on the anti-corrosive properties of Zn matrix.
Zn-Cr$_2$O$_3$ composite exhibited better microhardness and
thermal stability than Zn-Al$_2$O$_3$ composite coating. Zn- Al$_2$O$_3$
possessed better self-lubrication properties and hence better
tribological behavior. Therefore, it can be concluded that Zn-
Al$_2$O$_3$ composites are suitable for wide industrial applications
where the coatings are expected to perform under chemical,
thermal and mechanical demanding conditions. However, Zn-
Cr$_2$O$_3$ is limited to industries that require the coatings for their
mechanical properties only.

Acknowledgements

This material is based upon work supported financially
by the National Research Foundation. The equipment support
by Surface Engineering Research Centre (SERC) Tshwane
University of Technology, Pretoria is deeply appreciated.

REFERENCES

(2011).
1443(2008).
Sci. 9, 885-3903 (2014).
(2012).
[18] H.B. Hassan, Z. Abdel Hamid, Int. J, of hydr. energy, 36, 5117-
5127 (2011).
(2012).
Mat. and Des. 32, 4054-4061(2011).
[21] S. Srikomol, P. Janetaisong, Y. Boonyongmanera, R.
Techapiesancharoenki, Ach. Met and Mat, 59, 1287-1292
(2014).