Comparative Studies of Microstructural, Tribological and Corrosion Properties of Plated Zn and Zn-alloy Coatings

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Difficulties in choosing appropriate material(s) for a particular application and the control of environmental menaces cannot be over emphasized. Films of Zn and Zn–Al were electrodeposited on mild steel substrates using Zn and Zn–Al alloy plating solutions respectively. Focus ion beam scanning electron microscope (FIB-SEM) images and Atomic force microscope (AFM) were used to study the surface morphology, the topography and the surface adherent properties of the coatings. The elemental composition and the phases evolved in composite coatings were measured by means of X-ray diffractometer (XRD) and energy dispersive spectrometer (EDS). The cyclic voltammetry techniques were used to explain deposition process. The microhardness measurements and the electrochemical and wear behaviours of the deposits were investigated. Experimental results showed that Zn-Al coatings had homogeneous distribution of the fine particles deposited. These coatings had higher corrosion and wear resistances over the Zn deposited coatings as well as the substrate.

Keywords: Electrochemical study, AFM, composite, deposition, topography

1. INTRODUCTION

Since the invention of electrolytic plating technology, electrolytic metal coatings have been used in many fields due to their unique properties [1–5]. Electrolytic composite plating is a surface treatment technology developed on the basis of electrolytic metallic plating [6-10]. Zinc has been the most widely used electrodeposited metal for protecting steel against corrosion. The corrosion resistance it offers meanwhile is limited. Recently, significant efforts to improve the hardness, corrosion and wear resistances of pure zinc plating, can be traced towards alloying it in combination with different metals [11-18]. The choice of alloying metal differs from the electrolyte system used. It is also known, in particular, that the mechanical, physical and electrochemical properties of materials

can be improved by alloying metallic powder on the material of interest [13-18]. Due to this improvement, alloys such as Zn-Co, Zn-Fe, and Zn-Ni have tremendously gained a wider range of applications in both manufacturing and marine industries lately as a better substitute for ordinary zinc plating [19-25]. Although these coatings provide some advantages over zinc, but most of the time they cannot cathodically protect steel substrates in all kinds of natural atmospheric environments [22-25]. Electrochemically deposited zinc/aluminum alloy have greater corrosion stability as compared to thermally obtained Zn-Al alloy [6-8]. Meanwhile, it is difficult to carry out conventional chromate treatment on the surface of steel plated with an aluminum-zinc alloy containing 55% Al but a novel chromating solution containing an additive which acts as activating and oxidizing agent is effective in forming a dense chromating film for the protection of most surfaces [9]. Recently, successful electrodeposition of zinc-aluminum coating on mild steel were carried out with the help of aluminum tri-chloride on the zinc-aluminum deposition on the rest potential of golden and non-chromates zinc-aluminum [9].

In work presents detailed comparison of the microstructural, hardness, wear and corrosion properties of plated Zn and Zn-Al coatings on mild steel will be studied for the purpose of material selection.

2. EXPERIMENTAL PROCEDURE

2.1. Electrodeposition process

A new electro-deposition condition to produce Zn-Al coating was developed on mild steel. Nitric acid and sodium hydroxide was used for the dissolution of the metallic powders that constitutes the bath to form solutions containing Zn and Al ions. Deposition was achieved by adding gradually the measured mass of sodium hydroxide content which initiates paste that was admixed on the working bath as electrolyte. The chemicals used were of Analar grade and easily soluble in water. Distilled water was used for the preparation of solutions. The bath contain 50 g each of 98.5 % pure aluminum and 98.8 % zinc powder which were put into a 250 ml bottom flask and dissolved in 50 ml of NaOH, 50 ml of 5 % nitric acid respectively. The deionized water was added to the Al and NaOH gradually to form a paste before uniformity in the resulting solution was achieved. The investigation was carried out in three processes; pre plating process, plating process and the post plating process. In the pre plating process, the surface preparation was done on the polishing machine with different grades of emery paper in order of 60 μm, 120 μm, 360 μm, 400 μm and 1600 μm grades. Water was added intermittently so as to cool down the metal samples. During the grinding operation, the metal samples were rotated at an angle of 90° or 180° at intervals so as to erase previous marks which arose due to the initial grinding. The pickling of the samples was done in diluted HCl acid solution; this was to remove all organic contaminants and oxides, followed by electrolytic degreasing. This was carried out by treating the surface of samples with alkaline solution by passing current into the solution for about 5 minutes and subsequent cleaning in water, to remove all grease or oily contaminants.

In the plating process, the standard cell of 267 ml capacity was used. The electrolytically degreased metal substrate was immersed in a solution containing dissolved Zinc - Aluminum admix

salts and hydroxide bath and made the cathode by connecting it to the negative terminal of the rectifier of the electroplating bath. The anode was also immersed and connected to the positive terminal of the rectifier. The following plating parameters were varied, the voltage was kept at1.0 V for 20 minutes. More so, the immersion depth was kept constant. Finally, the samples were rinsed in water to wash the salt solution off the samples plated immediately after the electroplating process. The rinsing was done in distilled water for 5 seconds then later air dried.

2.2. Characterization of the electrodeposited samples

The electrodeposited materials preparation for characterization was done on the surface. Samples were cut to reveal their cross sections with a Struers Discotom-2 cutting machine.

Careful surface preparations are needed to reveal the important details of the microstructure evolved as a result of electrodeposition. Samples were prepared for metallographic examination. Metallography is the study of the physical structure and components of metals, typically using microscopy. The surface of a metallographic specimen is prepared by various methods of grinding, polishing, and etching. After preparation, it is often analyzed using optical or electron microscopy. Samples were ground from 80 to 1200 grit on SiC paper. The samples were then polished using diamond impregnated clothes of 3 μm down to 1 μm followed by an oxide polishing (OP-S) system. In the OP-S system, polishing is achieved through a combination of chemical treatment and gentle abrasive action, and it allows microscopic observations and characterization.

2.3. Electrochemical test

Linear potentiodynamic polarization tests were carried out on the Zn and Zn-Al deposited samples as well as the as-received sample.

Measurements were done using an Autolab potentiostat (PGSTAT30 computer controlled) with the General Purpose Electrochemical Software (GPES) package version 4.9. Measurements were made at room temperature using 3.65% NaCl solution. The solution for this study was prepared from analytical grade reagents and distilled water. An electrochemical cell consisting of working electrode (samples) graphite rods as the counter electrodes and a silver/silver chloride 3 M KCl electrode as the reference electrode (SCE). The corrosion potential (E_{corr}), and corrosion rate were determined accordingly. The specimen was scanned from a potential of −1.51 V.

3. RESULTS AND DISCUSSION

### 3.1. Comparison studies of Zn and Zn-Al based depositions

3.1.1. Surface morphology

Figures 1 and 2 shows the Focus ion beam scanning electron micrographs of Zn-Al and Zn coatings respectively. From the FIB-SEM micrographs of the two different samples under

investigation, the electrodeposition of Zn-Al powders brought about good surface finish on mild steel as a result of the uniform dispersion achieved.
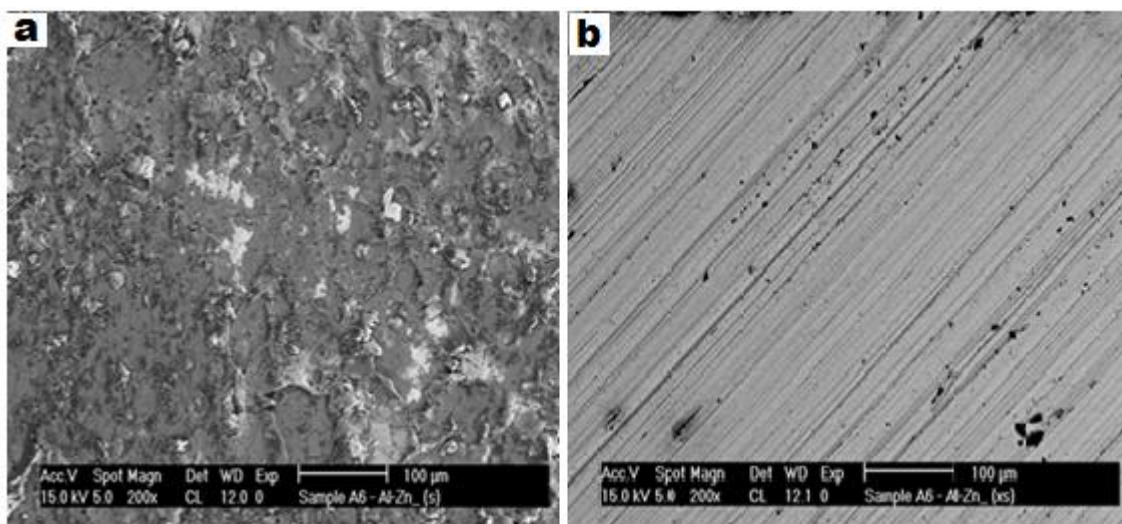
Figure 1. Scanning electron micrograph of Zn-Al sample showing (a) the surface and (b) cross section morphology of the coating.
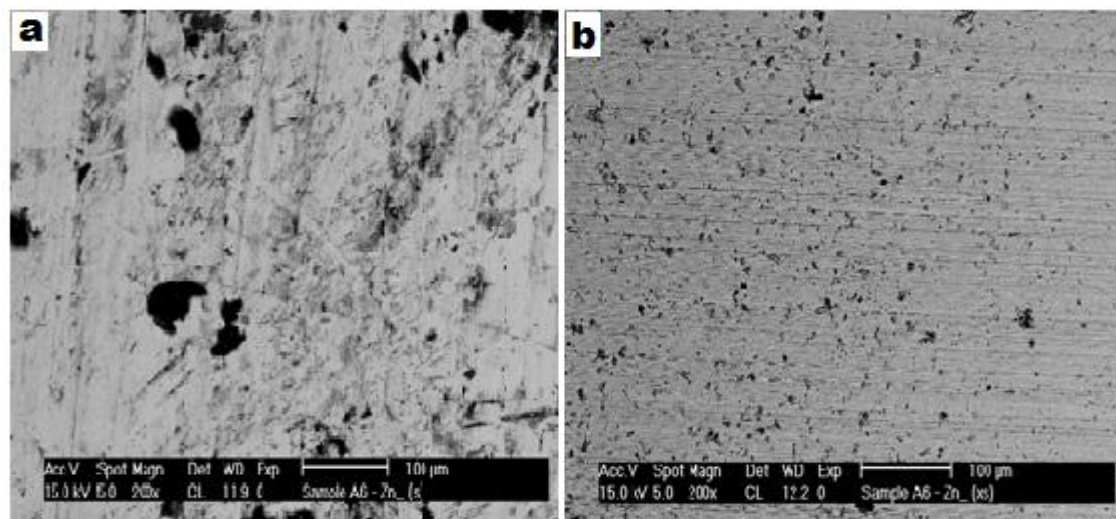

Figure 2. Scanning electron micrograph of Zn sample showing (a) the surface and (b) cross section morphology of the coating.

However, for the Zn deposition, the dispersion was quite uniform but microstructure had some few solid crystals embedded at the surface of the substrate. Al distribution within the steel matrix resulted in good surface finish; and its high affinity for oxygen resulted in formation of Al_2O_3 oxide film on the surface which led to good resistance to corrosion attack and finer microstructure (22, 24 and 25). Surface stability of Zn-Al and ordinary Zn coated samples was confirmed by the cross

sectional micro-graphical study and EDS, with aluminum still maintaining its adhesion properties. The nature of crystal growth with the presence of Al in zinc bath at 1 V was explained with the help of atomic force microscope photomicrographs.

AFM photomicrographs as shown in Figures 3 and 4, indicates fine grain size, uniform arrangement and crystal growth for the Zn-Al coating. Unlike the ordinary Zn deposition where good surface deposition was achieved but irregular or inhomogeneous dispersion of deposit was observed.
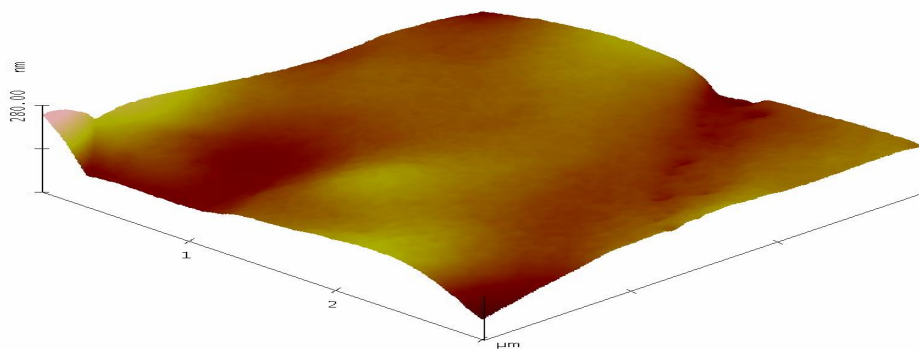
Figure 3. AFM of Zn-Al coating showing deposited surface topography and distribution
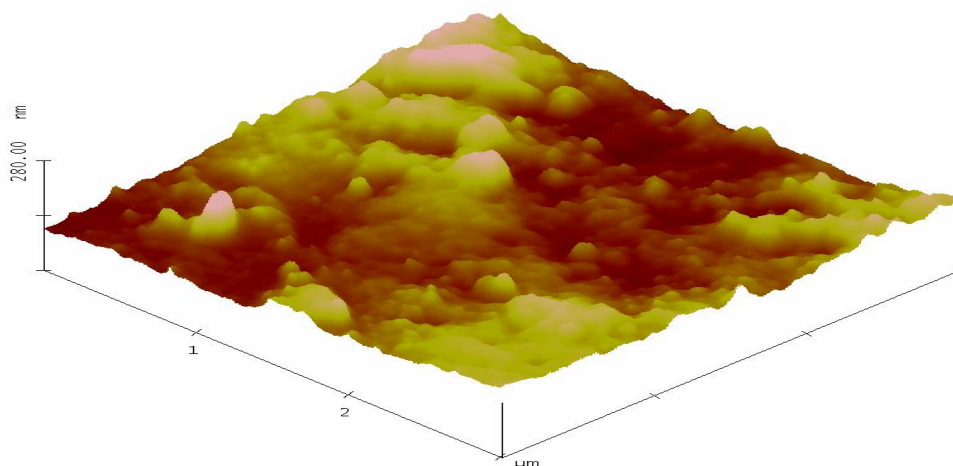
Figure 4. AFM of Zn coating showing deposited surface topography and distribution

3.1.2. Weight gain and surface adhesion

Distinctive difference can be seen from the result of analysis of Zn and Zn-Al on mild steel. Table 1 shows the variation of weight gain as a function of applied voltage for Zn and Zn-Al coatings of some selected samples.

Table 1. Comparison of Zn and Zn-Al plated samples.

Sample No	Samples in voltage	Zn-Al Weight/Thickness of deposition	Zn Weight/Thickness of deposition
1	1.0	0.400/8.43	0.395/8.40

Although the increase in weight gain and deposition thickness for Zn-Al coatings is small but it is very visible starting from the initial stage of electrodeposition. The thickness increases as the voltage of deposition increases. It was observed that the increase in weight was due to the bonding and electron transferring properties of Al ion. Aluminum being a light metal displayed faster transfer of the Al^{3+} much more than Zn^{2+} ion with formation of stable properties. Visual inspection of the Zn plated samples revealed few traces of deformation after deposition, compared with Zn-Al with the perfect matrix bonding formed. The Zn-Al deposit is uniformly and evenly distributed in the Fe-matrix. According to (9 & 10) the crystallization of electrodeposited layer is a very important step for the electrogrowth, since it influenced directly the structure of the deposit and therefore its weight property. In view of this, it is important to say that the weight gain and the pore free nature of deposited Zn-Al is directly related to the small grain size of the Al particles and of course the influence of deposition rate.

3.1.3. Corrosion resistance

Comparative electrochemical studies between Zn-Al, Zn deposited and the as-received samples were carried out. The results of polarization measurements for all three samples investigated are summarized in Table 2.

Table 2. Summary of the potentiodynamic polarization results

Sample	i_{corr} (A)	I_{corr} (A/cm^2)	R_P (Ω)	E_{corr} (V)	Corrosion rate (mm/yr)
Zn-Al	5.74×10^{-8}	3.52×10^{-7}	1.38×10^{5}	-0.768	2.0×10^{-7}
Zn	2.71×10^{-6}	1.77×10^{-5}	4.56×10^{2}	-1.004	6.6×10^{-2}
As-received	2.04×10^{-3}	7.04×10^{-2}	2.76×10^{2}	-1.536	41

Figure 5 shows the anodic polarization curves for the samples. The E_{corr} recorded for Zn-Al deposited sample is three orders of magnitude higher than that of the substrate and two orders of magnitude higher than that of the Zn deposited sample. Based on E_{corr} values alone, the Zn-Al sample is more corrosion resistant than the untreated steel because of increased E_{corr} value.

The anodic corrosion current densities (I_{corr}) of the as-received; the Zn and Zn-Al samples are 7.04×10^{-2}, 1.77×10^{-5} and 3.52×10^{-7} A/cm^2 respectively. This means that a five order decrease in magnitude of the corrosion current density was attained after electrodeposition of Zn-Al on mild steel. This was attributed to the presence of Al within the matrix of mild steel.
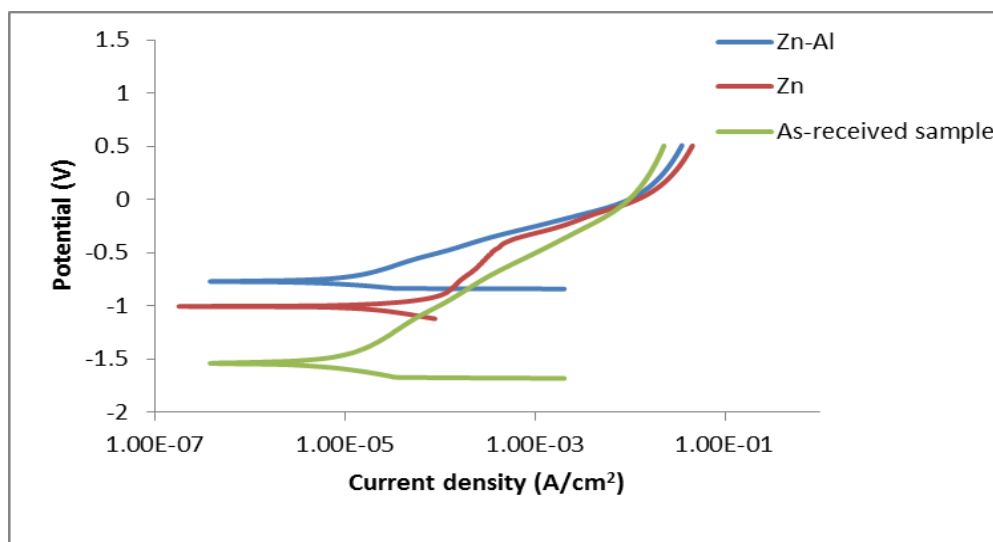
Figure 5. Potentiodynamic polarization curves for as-received Zn and Zn-Al coatings

In the same way, the Zn-Al sample was found to exhibit corrosion rate well below that of the untreated and the Zn deposited samples. Zn-Al sample was observed to display the lowest corrosion rate of 2.0×10^{-7} mm/yr. If this is compared with the corrosion rate of mild rate 41 mm/yr, a significant decrease in the rate of corrosion was achieved as a result of electroplating. Based on this, the Zn-Al coating is much more corrosion resistant than the substrate and the Zn coating.

According to (14, 15, 17 and 18) electrochemical examination of reinforced aluminum stated that the materials with the highest polarization resistance R_p (slope of the Tafel plot) and the lowest corrosion current i_{corr} have the highest corrosion resistance than the other materials. R_p for the mild steel and the Zn and Zn-Al samples are 2.76×10^2, 4.56×10^2 and 1.38×10^5 Ω while their corrosion currents are 2.04×10^{-3}, 2.71×10^{-6} and 5.74×10^{-8} A respectively. In these two cases Zn-Al sample exhibited the highest R_p as well as lowest corrosion current, therefore considering these with other parameters such as E_{corr}, I_{corr} and the rate at which Zn-Al sample corrodes, this sample exhibited the highest corrosion resistance in the test solution. This means that a geometric decrease in magnitude of the corrosion rate was attained after Zn-Al deposition. This may be attributed to the presence of the aluminum oxide film present within the zinc region in the matrix of substrate which is also in agreement with the prediction of the past author.

3.1.4. Wear resistance

The wear scar morphology of the Zn-Al and Zn deposited steels were used to establish the stability of deposit on the substrate. Figures 6 and 7 shows the worn surface observed after selected wear time on Zn-Al and Zn samples respectively. It can be seen from the scars, that severe degree of plastic deformation, massive grooves, pits and fracture dominated the surface of the Zn deposited sample.
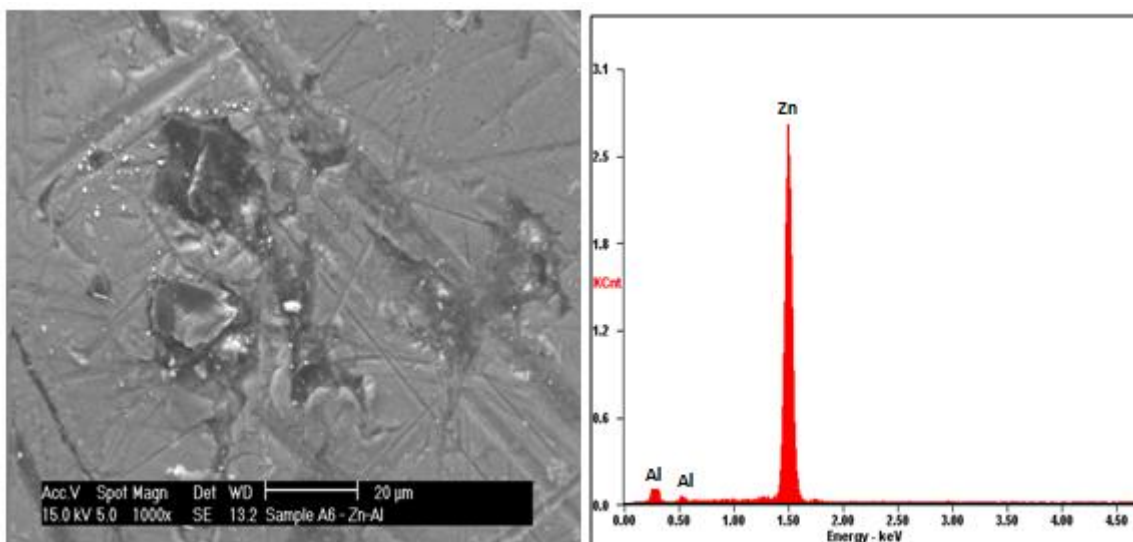
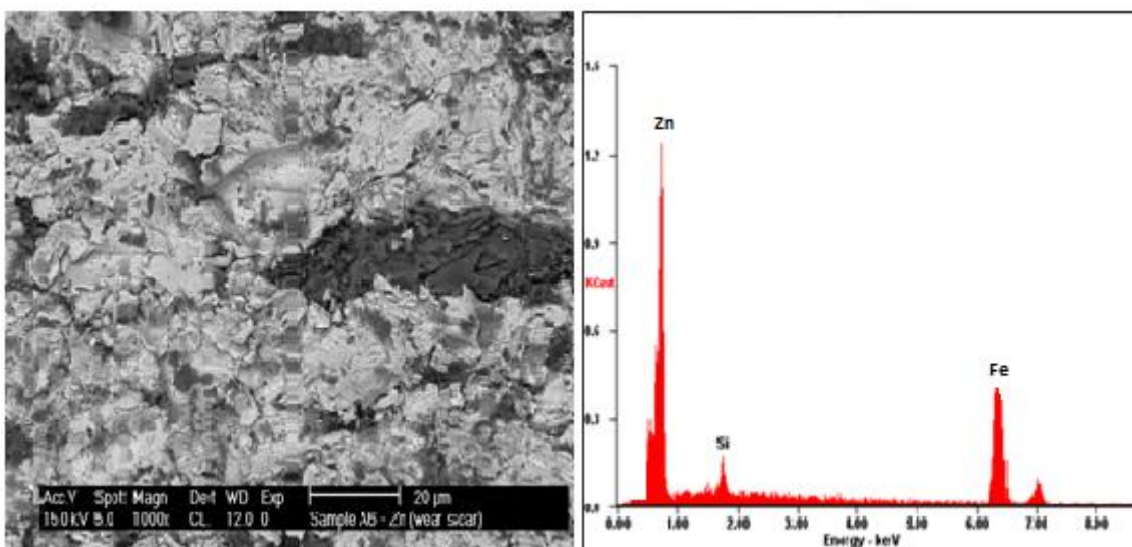**Figure 6.** SEM/EDS images of the wear scar of Zn-Al deposit

Figure 7. SEM/EDS images of the wear scar of Zn deposit

This is due to the slightly weak adhesion between the Zn deposit and the steel. This may be expected due to the examination of some author in this regards (6, 16, 24 and 25). Contrary to the above, lesser degree of plastic deformation, grooves and little pull-out can be seen on the Zn-Al deposited samples. In addition, it is seen that the width and depth of the wear scars on the Zn-Al sample are much smaller than that of the Zn sample under the same wear conditions. It should be noted that the stable cohesion have a better flow than the visible irregular degradation incurred by ordinary zinc coating. Thus, indicating that Zn-Al sample exhibit mild abrasive wear. The graph of the variation of the wear rate as a function of time for the three samples (as-received, Zn and Zn-Al depositions) can be seen in Figure 8. Comparison of the experimental results show that wear rate was remarkable. The

rate of wear increase is very high for the as-received sample; on other hand, the rate of wear is very low for the Zn-Al sample.

The wear rate of as-received sample shows poor wear resistance which is expected. The wear rates of Zn deposited sample indicated a tremendous improvement compared with the as-received. However, Zn-Al sample yields a better wear resistance which can be attributed to the aluminum inclusion. Therefore, addition of aluminum to zinc improved the properties of the substrate as observed in the SEM images above.
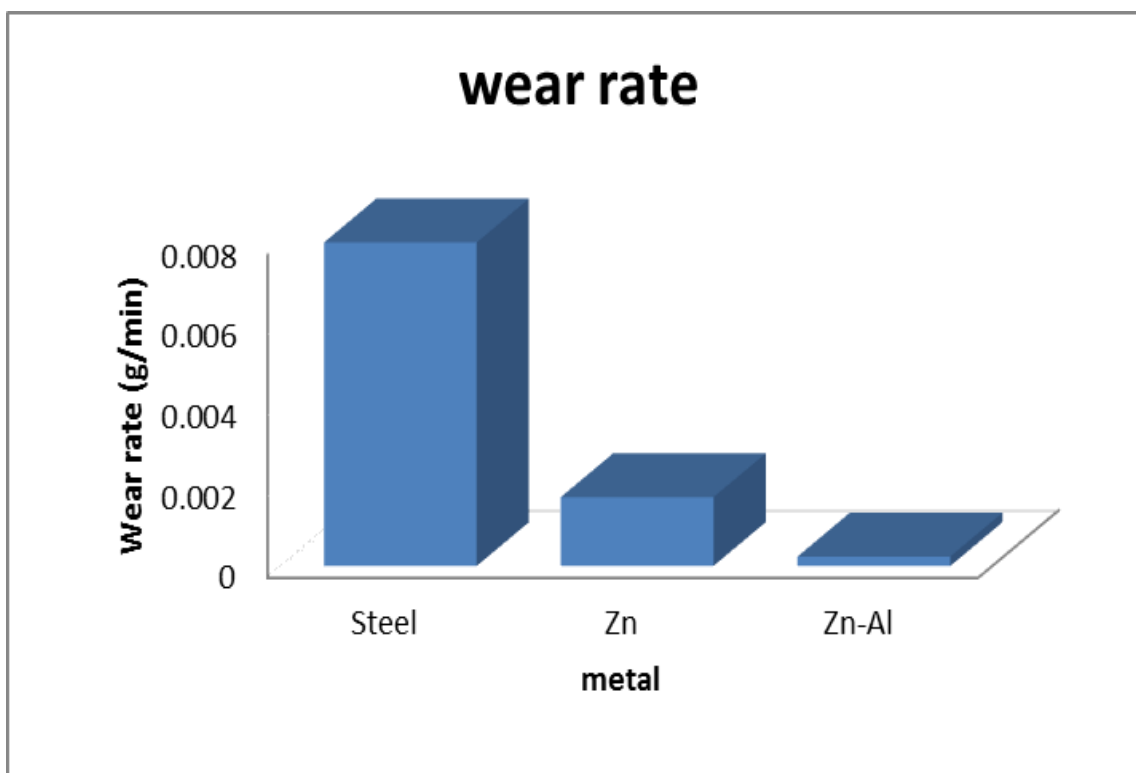

Figure 8. Variation of wear rate with time

3.1.5. Hardness Property

With the Vickers microhardness tester, the microhardness/depth profiles for the as-received, Zn and Zn-Al samples tested were plotted (Figure 9).

A good increase in the microhardness value was observed in the Zn-Al coating as shown in the Figure above. The microhardness value for the substrate material was 55.28 HVN, for the Zn coating was 108.30 HVN and for the Zn-Al coating the microhardness value was 137.14 HVN. It can be inferred that over 100% increase in the value of the microhardness was achieved regardless of the electrodeposition material. However, electrodeposited surface coatings with Zn-Al admix material resulted in the highest microhardness value which is about 148% increase. The increase in hardness of the Zn-Al coated specimens was due to the presence of the Al as reinforcement additive.
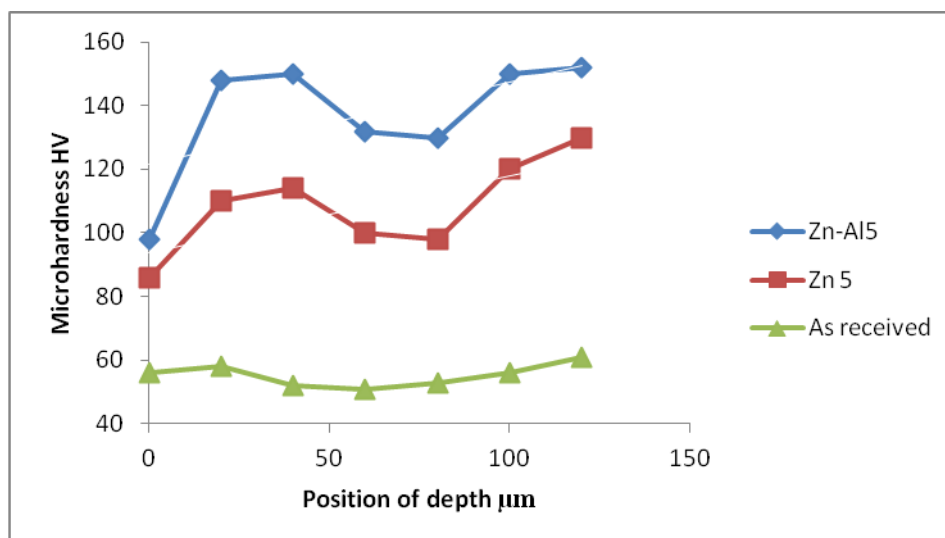
Figure 9. The microhardness/depth profile for Zn and Zn-Al coatings

4. CONCLUSIONS

Electroplating of Zn and Zn-Al were perfected carried onto the surface of mild steel substrates. The Al codeposition with Zn has significantly enhanced surface adhesion property and improved the stability of mild steel compared to ordinary zinc deposit. The consequence of applied voltage, regulates the uniform arrangement of crystals resulted in fine grained deposits and hence the following improvements in properties:

➢ *Increment of Microhardness Property:*

Mild steel: 55.28 HVN

Zn deposition: 108.30 HVN (Power - 1 V; time - 20 min)

Zn-Al deposition: 137.14 HVN (Power - 1 V; time - 20 min)

It is worthy to know that Al particles during deposition of Zn-Al greatly increased hardness property of the coating. Percentage increment of hardness is of the order of 148%.

➢ *Increment of Corrosion Resistance:*

For Zn deposition: A substantial improvement was attained with sample plated for 20 minutes; and 1.0 V. For Zn-Al deposition, the best corrosion resistance of the coatings was also obtained at the same plating parameters. Which indicates clearly that Zn-Al coatings displayed higher resistance to corrosion attack than the ordinary Zn deposition and the as-received mild steel substrate. It can be inferred that severity of attack reduces considerably due to the surface adherent bond between zinc and aluminum and the substrate. More so, Al itself possesses good resistance to corrosion in the atmospheric environment.

➢ *Increment of Wear Resistance:*

Significant improvement in the wear resistance of mild steel was achieved as a result of electroplating. The Zn-Al alloys showed higher wear resistance as compared with the Zn deposited and the as-received mild steel. Because of the extremely fine microstructure, excellent smearing

characteristics, less groove were given rise to. Percentage increment in wear resistance of mild steel in about 98%.

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