PROPERTIES EVALUATION OF TERNARY SURFACTANT-INDUCED Zn-Ni-Al$_2$O$_3$ FILMS ON MILD STEEL BY ELECTROLYTIC CHEMICAL DEPOSITION

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The present study was aimed to develop a multilayer-modified coating that will enhance the surface characteristics of mild steel against chemical and mechanical deterioration with a ternary Zn-Ni-Al$_2$O$_3$ composition induced with monoethylanine (MEA) and triethylanine (TEA) as surfactant using electrolytic chemical deposition. The microstructures of the coated-body was characterized by X-ray diffractometry (XRD) and scanning electron microscope equipped with electron dispersive spectroscope (SEM–EDS). Equally, the adhesion and topography of the coating was examined with atomic force microscopy (AFM). The assessment of the micro-hardness and corrosion properties of the developed composites were used as a criteria. From the results, the deposition of admixed Zn-Ni-Al$_2$O$_3$ ternary composite particles in the presence of bath-additive surfactant on to the substrate was significantly enhanced. The corrosion resistance of the coated surface was also improved. There exist an improvement in the structural modification and better interfacial adhesion of coatings on the substrate upon addition of TEA and MEA as surfactants during the deposition process along with the electro-deposition variables considered.

1. Introduction

Electro-deposition composite coating on metal surface has gained attention in recent time due to the advantages derived therein; such as wear resistance, self-lubricating, corrosion or oxidation resistance [1]. Mild steel have been known to have wide range of industrial application because of its easy availability, ease of fabrication, low cost and good tensile strength among others [2-5]. However, in some service conditions its functionality and durability are subject of concern due to corrosion and mechanical deterioration [5, 6]. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating [7, 8]. Zinc also corrodes in solution having pH lower than 6.0 and higher than 12.5, while within the range corrosion is very slow. Though, zinc is anodic to steel, it protects the base metal even when the deposit is porous [5]. An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency. Equally, Zn-Ni alloy coatings have been reported to be widely used on steel substrate which have better corrosion resistance than Zn deposit alone [9] and to improve corrosion resistance in automobile industry [9, 10]. The authors studied this binary alloy with Al$_2$O$_3$ in nanoparticle form. However, good deposition depends mainly on the nature of bath [11-13]. However, for the purpose of improving the corrosion, wear, hardness and thermal properties of this coatings, the use of ceramics based admixtures have been suggested [14-16]. In addition,

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bath additives, surfactant and nano-particle have been during electro-deposition to further enhance bright bath formulation [17, 18]. Aluminium oxide (Al_2O_3) as ceramic additive is mostly to changes and cause the preferred deposit orientation that could enhance mechanical features of the coating. In this work an attempt was made to evaluate the properties developed as a result of inducing triethylanine (TEA) and monoethylanine (MEA) as essential additive in electro-deposition of $Zn-Ni-Al_2O_3$ film on mild steel obtained from an alkaline chloride bath using an electrolytic chemical deposition techniques.

2. Experimental procedure

2.1 Preparation of substrate

The dimension of the mild steel (substrate) used was 40 mm x 20 mm x 1 mm sheet and zinc sheets of 30 mm x 20 mm x 1 mm were prepared as anodes. The mild steel specimens' chemical composition is shown in Table 1. The cathode was mild steel coupons and anode was commercially pure zinc (99.99%). The mild steel specimens were polished mechanically, degreased and rinsed with water as described [19].

Table 1: Nominal chemical composition of mild steel substrate used (wt%)

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

2.2 Formation of deposited coating

The mild steel substrate earlier prepared was actuated by dipping into 10% HCl solution for 10 seconds followed by rinsing in distilled water. Analar grade chemicals and distilled water were used to prepare the plating solution at room temperature. Prior to plating, the TEA and MEA were added to the prepared $Zn-Ni-Al_2O_3$ particles electrolytic solution as shown in Table 2. The formulations were then heated to 40^OC to easy admix and dissolution of any agglomerate in the bath solution. The bath produced was stirred continuously as heating trend lasted for hours before plating.

Table 2: Bath composition of $Zn-Ni-Al_2O_3$ ternary co-deposition induced with TEA/MEA surfactants

Composition	Mass concentration (g/L)
ZnCl	100
Ni_2Cl	100
KCl	80
Boric Acid	10
Glycerin	10
Al_2O_3	20
Tea	2
Mea	2
pH	4.8
Voltage	0.5-1.0V
Time	15 min.
Tempt	40^oC

2.3 Preparation of the coatings

The prepared $Zn-Ni-Al_2O_3$ composite in the presence of Tea and Mea was heated for 2 hr and periodically stirred to obtain a homogenous solution before electrolytic deposition process. The prepared cathode and anodes were connected to the D.C. power supply through a rectifier at a current of 2 A with varying applied voltage; 0.5 and 1.0 V for dwell time of 10 and 15 minutes. The distance between the anode and the cathode and the immersion depth was kept constant. Thereafter, the samples were rinsed in distilled water and dried.

Table 3: Formulated bath composition of $Zn-Ni-Al_2O$ induced with TEA/MEA surfactants.

Sample identification	Ternary/additive composition	Time of deposition (min)	Potential (V)	Current (A)
Blank	-	-	-	-
Sample 1	$Zn-Ni-Al_2O_3$+TEA/MEA	10	0.5	2A
Sample 2	$Zn-Ni-Al_2O_3$+TEA/MEA	10	1.0	2A
Sample 3	$Zn-Ni-Al_2O_3$+TEA/MEA	15	0.5	2A
Sample 4	$Zn-Ni-Al_2O_3$+TEA/MEA	15	1.0	2A

2.4 Characterization of the coatings

The surface appearance and morphology of the coating and thin films were characterize with TESCAN scanning electron microscope equipped with energy dispersive X-ray (SEM/EDX) and an optical microscope (OPM). EDAX point analysis was used to observe the elemental composition. The adhesion profile, topography and morphology of sample surface before and after coating was observed with the help of Atomic force microscope. The XRD spectral of some plated sample were assessed. High optic diamond based dura scan micro-hardness tester was used to estimate the average micro-hardness of the deposit in an equal interval range from an average of four measurements.

2.5 Photo-electrochemical measurement

The specimens were embedded in epoxy resin leaving a working area of 1.2 cm^2. The working surface was subsequently ground with grinding papers from 600 down to 1800 grit, cleaned by distilled water and ethanol. A conventional three electrode cell, consisting of saturated calomel (SCE), graphite, and coated MS as reference, auxiliary, and working electrode respectively, was used to study the electrochemical behaviour of the deposited sample and as-received mild steel in 3.65 wt. % NaCl solution. The electrochemical measurement was done with Autolab PGSTAT 101 Metrohm potentiostat/galvanostat. An electrolytic cell containing 50 ml of electrolyte, with and without plated sample, a graphite rod which works as auxiliary electrode and silver chloride electrode (SCE) as reference electrode were used. The potentiodynamic potential scan was fixed to run from -1.5V to +1.5 mV with scan rate of 0.012V/s. The electrochemical corrosion test was performed at room temperature in a static solution.

3. Results and discussion

3.1 Effect of Tea and Mea additive and electrolytic bath constituents

In the previous reports, coarse and dull deposit are produce without bath additives [20]. Since, additive especially surfactant have proven to provide good adhesion strength and refined

grains. TEA and MEA are used as intermediate and as a neutralizer for acid component in the corrosion prevention and emulsifiers. With 2 ml of each surfactant, a bright and adorable deposit was achieved at 15 minutes, 0.5 V. Equally, the coatings were found to display excellent properties in the presence TEA and MEA. The influence of KCl was to increase the conductance capacities of the bath formulation. In a homogeneous dispersion of the thin film formation over the interfaces, complexes are needed and boric acid/glycerine tends to function as such. This complexes act with ions of Zn^{2+}, Ni^{2+} and $Al^{3+,}$ Al^{2+} to reduce ionic tension of the cathode, provide grain refine and offer better adsorption on the cathode resulting to significant adherent and improved surface morphology.

3.2 Micro-hardness and photo-electrochemical studies

3.2.1 Micro-hardness studies

The effects of Zn-Ni-Al_2O_3+Tea/Mea at different applied voltage of 0.5 and 1.0 V in 15 minutes on mild steel is shown in Fig. 1. From the result, the micro-hardness increase with additive dispersed into the bath. The pronounced micro-hardness improvement with all sample upon applied potential suggests that Al_2O_3 have a significant strengthening effect. From previous report [20, 21], ceramics composite particles enhanced the grain structure and improve the micro-hardness of the composite coatings. Composite- Al_2O_3 thus change and cause smaller grain and provide structural modification which could enhance the hardness of the composite coatings [22, 23].
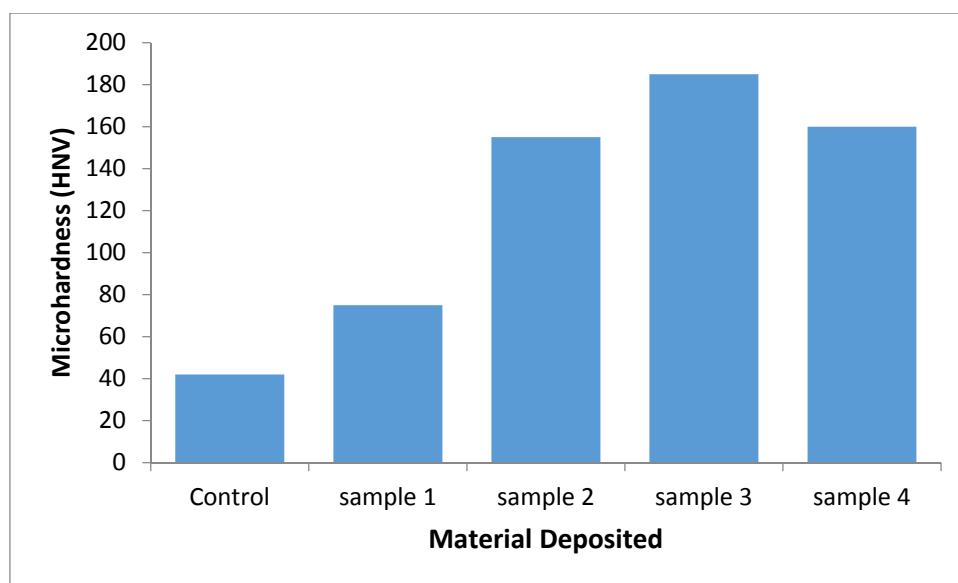

Fig 1: Variation of micro-hardness of deposited materials

3.2.2 XRD phase evaluation

Fig. 2 and 3 show the X-ray diffraction spectra of some coated samples with various phases. For example in Fig. 2 phases such as $ZnAl_2O_3$, $ZnAl_2Ni7$, AlNi and Zn_2AlO_3. Similarly, Al_2O_3 ZnO, ZnNiO, $Zn_2Al_2O_3$ and ZnO, NiO are predominant in Fig. 3 besides original Zn-Ni based particulate which was observed within coating interface. Higher peak of the resulting phases are as a results of the admixed particulate of Al incorporated resulted into co-deposition and in turn led to formation of high strength composite matrix. The interaction between Zn-Ni and Al_2O_3 ultimately produces a crystal orientation of grain size rather than chemical dissolution of Al in the admixed formation. Equally, the improvement of different crystal structures can be related to the growth of grains due to its compactness. In general, all the deposited samples provided a good reflection of surface structure expected within the phase.
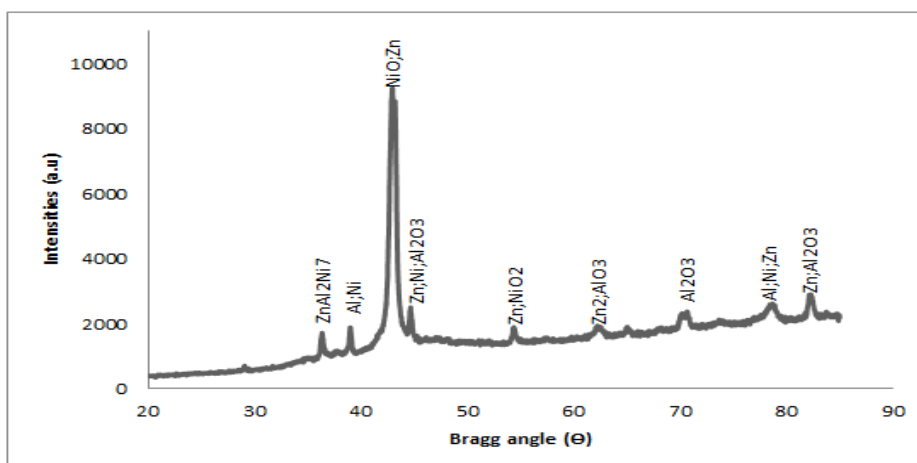
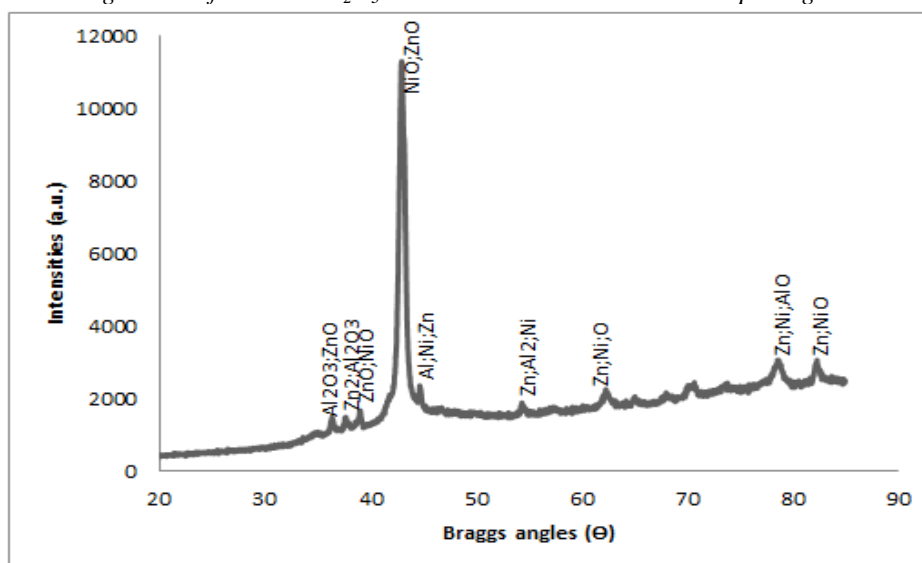*Fig 2: XRD for Zn-Ni-Al₂O₃+Tea/Mea at 0.5 V in 10 minutes plating time*

Fig 3: XRD for Zn-Ni-Al₂O₃+Tea/Mea at 1.0 V in 15 minutes plating time

3.2.3 Photo-electrochemical studies

The potentiodynamic polarization corrosion test was evaluated in 3.65% NaCl solution with the Tafel plots extrapolation for the coatings shown in Fig. 10. Linear potentiodynamic polarization data of coated and uncoated samples in a static 3.65% NaCl solution is shown in Table 4. In all cases, the potential of the developed coating matrix resulted in an increased corrosion potential than the as-received sample at -1.53900 mv. The corrosion rate and current density decreased significantly. It can be said that the developed ternary coatings improved the corrosion resistance of the mild steel with increased polarization resistance value. This indicates that the admixed coatings matrixes created a good bonding and adhesion with the substrate material. The coatings of the mild steel as a significant surface resistance to corrosion process, which in turn lower the corrosion rate. The polarization resistance of all the coated sample greatly improved in the following trend 1>3>4>2>As-received with the Rp values of 126.42Ω, 221.57Ω, 215.61Ω, 208.56Ω, and 27.6 Ω respectively.
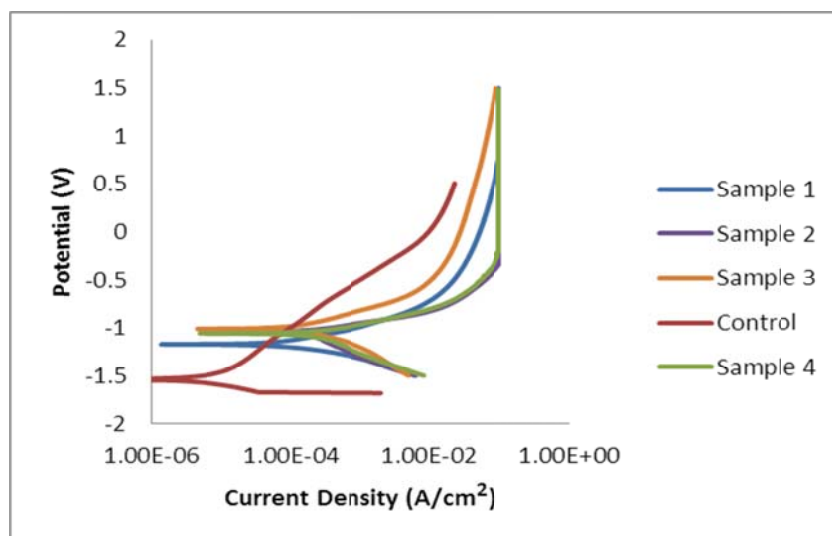
Fig 4: Linear Potentiodynamic Polarization curve of coatings and uncoated samples in 3.65% NaCl solution

Table 4: Linear Potentiodynamic Polarization Data of coated and uncoated samples in a static 3.65% NaCl solution

Sample No	Ecorr, Obs (V)	jcorr (A/cm²)	icorr (A)	CR(mm/yr)	Rp (Ω)
4	-1.0563	5.63E-05	5.63E-05	0.65385	215.61
3	-1.0103	4.70E-05	4.70E-05	0.54663	221.57
2	-1.1699	6.37E-05	6.37E-05	0.74046	208.56
1	-1.0446	6.79E-05	6.79E-05	0.78867	126.42
As-received	-1.5390	7.04E-02	2.04E-03	4.10000	27.600

3.3 SEM/EDS surface characterization of deposited sample and their AFM analysis

3.3.1 SEM/EDS surface characterization

In Fig. 5-9, the SEM/EDS of Zn-Ni-Al$_2$O$_3$+TEA/MEA 10 min at 0.5 V, Zn-Ni-Al$_2$O$_3$+TEA/MEA 10 min at 1.0 V, Zn-Ni-Al$_2$O$_3$+TEA/MEA 15 min at 0.5 V and Zn-Ni-Al$_2$O$_3$+TEA/MEA 15 min at 1.0 V respectively. In general it can be seen that the thin film formed on the mild steel plate resulted into a good appearance, better plating and good adhesion. The nature of the surface morphology and orientation in Fig. 6 unveiled the non-homogeneous appearance but good dispatches as expected. For that reason, the observed improvement may not be far from the possibility that the deposition behaviour and the adhesion strength of any particular plating often based on the potential, current density and the most especially the time of deposition [24]. In Fig. 6, the decreased hardness may be attributed to the fact that the time of deposition and the potential involved (0.5 V, 10 min) does not give sufficient plating as compare to that of (Zn-Ni-Al$_2$O$_3$+TEA/MEA 15 min at 0.5 V and Zn-Al$_2$O$_3$+TEA/MEA 15 min at 1.0 V) as shown in Fig. 8 and 9.
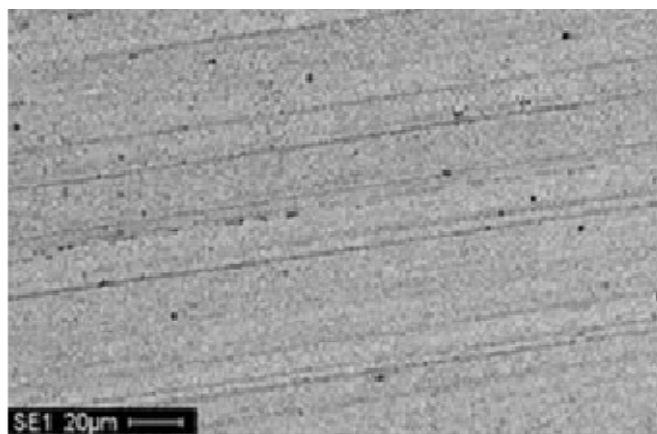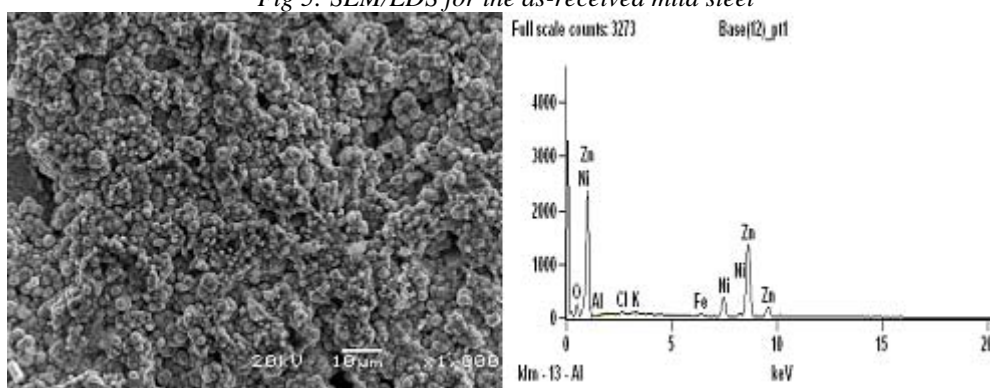
Fig 5: SEM/EDS for the as-received mild steel

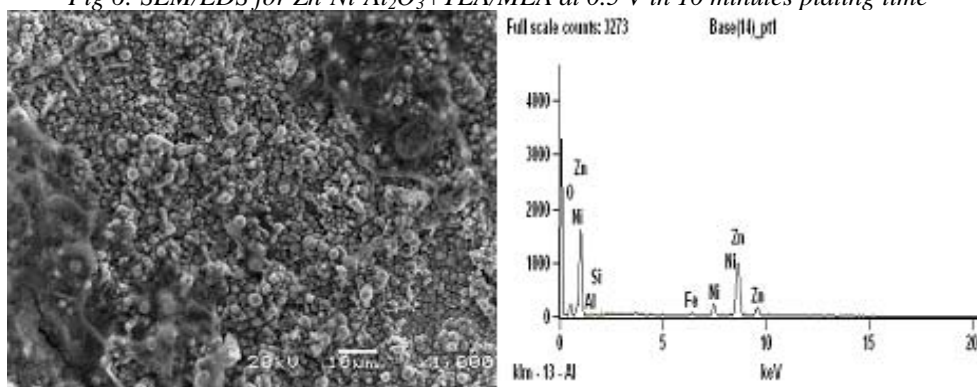*Fig 6: SEM/EDS for Zn-Ni-Al$_2$O$_3$+TEA/MEA at 0.5 V in 10 minutes plating time*

Fig 7: SEM/EDS for Zn-Ni-Al$_2$O$_3$+TEA/MEA at 1.0 V in 10 minutes plating time
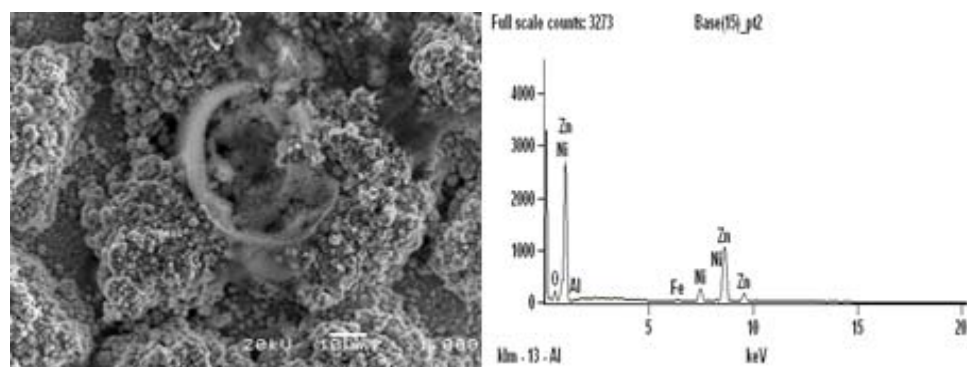

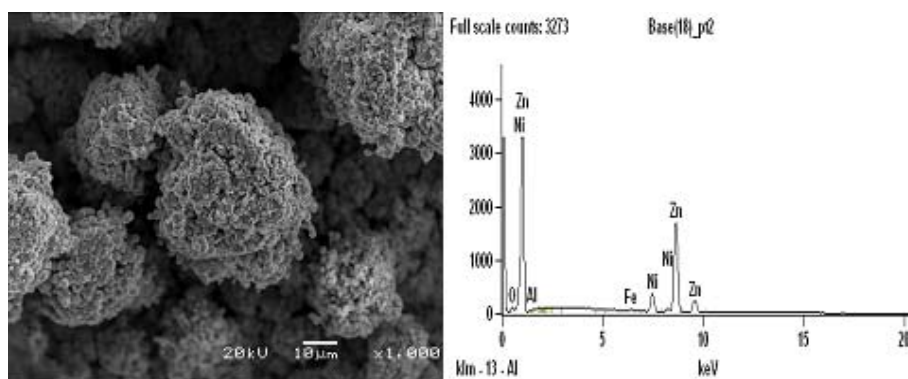*Fig 8: SEM/EDS for Zn-Ni-Al$_2$O$_3$+TEA/MEA at 0.5 V in 15 minutes plating time*

Fig 9: SEM/EDS for Zn-Ni-Al$_2$O$_3$+TEA/MEA at 1.0 V in 15 minutes plating time.

The introduction of the surfactant via bath co-deposition; TEA and MEA resolve stress behaviour that might occur during the coating due to the relieve agent with better adhesion within the interface due to boric acid and the conductance. No few porosity of coating could be observed in Fig. 8 and 9 and the Al$_2$O$_3$ composite intermediately connect properly with zinc-nickel interfaces. Within all micrographs (Fig. 5-9), evidence of moderate adhesion and elemental plating constituent are shown. Though the presence of Al$_2$O$_3$ provides more nucleation sites and retards the crystal growth [25]. One great characteristic of Zn-Ni-Al$_2$O$_3$ in the presence of Al$_2$O$_3$ was the uniform and continue thickness without a flaws. The absence of this defects and flaws along the interface is significant in this study and is an indication of good coating matrix and good adhesion properties.

3.3.2 Atomic Force Microscopy (AFM) Analysis

AFM was performed on Zn-Ni-Al$_2$O$_3$ obtained at 0.5 and 2V deposition condition as shown in Fig. 10. In all alloy deposited, uniform crystallites coalesced with small grain were found affirming the result obtained from scanning electron micrograph; the topography of the Zn-Ni-Al$_2$O$_3$ matrix with Al$_2$O$_3$ additives show better adhesion behaviour.
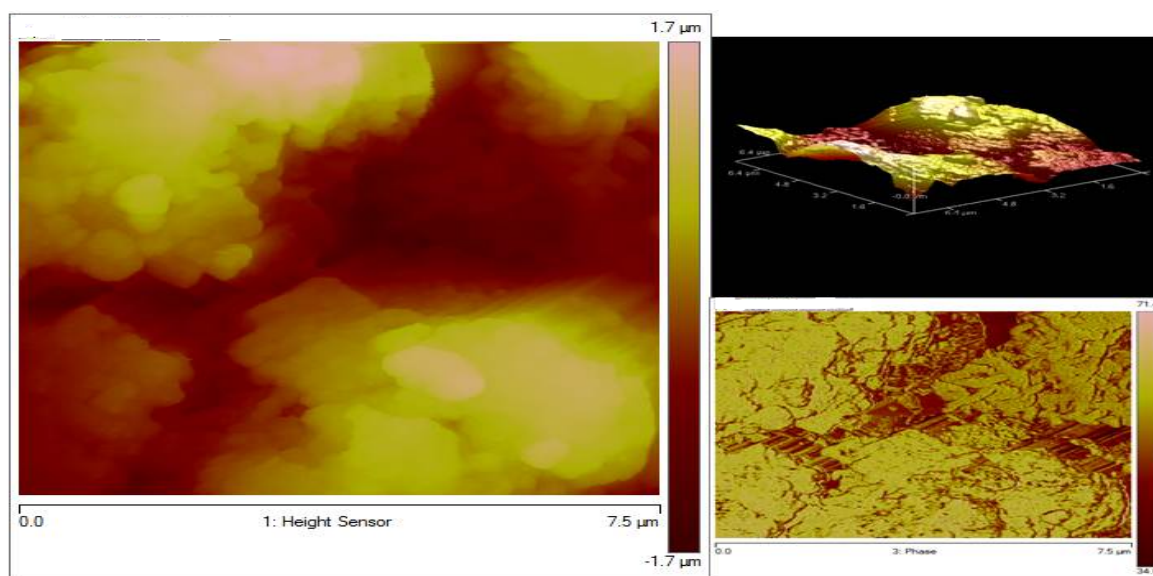

Fig 10: AFM image of Zn-Ni-Al$_2$O$_3$ film with TEA/MEA obtained at 0.5 V for 15 min showing a 3D topography and adhesion view

4. Conclusions

The mixed Zn-Ni-Al$_2$O$_3$ in the presence of TEA and MEA organic additive by electrolytic co-deposition technique have been deposited on mild steel substrates successfully

In general TEA/MEA, Al$_2$O$_3$ and particulate contribute immensely to the hardness behaviour of the Zn-Ni-Al$_2$O$_3$ films coatings and hence the non-existence of cracks and flaw indicating a well adhered coatings on the substrate giving rise to better hardness and corrosion resistance.

The XRD spectra of the developed thin film showed that Zn-Ni-Al$_2$O$_3$ alloy coatings consisted of strengthening phases such as Zn$_2$Al$_2$O$_3$, ZnAl, AlNi, Zn$_3$Al$_2$ and ZnAl$_2$Ni7 predominantly.

From the morphological, hardness and electrochemical studies, Zn-Ni-Al$_2$O$_3$+TEA/MEA 15 min at 0.5 V alloy coating have demonstrated better performance than other coatings in terms of hardness and surface appearance.

Acknowledgements

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