

Short Communication

Effect of Process Parameter on the in-situ Intermetallic Composite Coating and Microstructural Evolution of Zn-Al₂O₃ in the Presence of TEA/MEA on Mild Steel

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Zn-Al₂O₃ composite coating electrodeposits have been produced from chloride bath in the presence of Triethanolamine (TEA) and Monoethanolamine (MEA). The plating effect of TEA and MEA as addition agent on the Zn-Al₂O₃ alloy is investigated using SEM/EDS, x-ray diffraction (XRD) and atomic force microscope (AFM). The mechanical properties were examined through micro-hardness tester. The presence of TEA and MEA as a surface-active additive is also felt to accompany the performance of the fabricated coating. The SEM results for Zn-Al₂O₃ deposits in the presence of TEA/MEA indicate that surface-active additive have a strong influence on the deposit surface morphology and improved micro-hardness behavior which is assisted by the change in the deposition process parameter.

Keywords: Structural modification, Corrosion resistance, Surface-active additive. SEM

1. INTRODUCTION

Almost all industries and household use minor or enormous quantity of mild steel. This describes its huge importance to major engineering sector [1-6]. Its cost factor and availability has been described as a prime advantage over other metals. Meanwhile, the problem of mild steel is vested in corrosion and mechanical deterioration behaviour [3, 6-9]. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating [10-15]. 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 [5-6]. An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency. However, good deposition depends mainly on the nature of bath, [16-20]. To enhance zinc coating several researchers from literature have established the use of composite coating as a desirable replacement for ordinary zinc coating. Composite based depositions are increasingly used for a range of manufacturing applications to offer wear and hardness protection, corrosion resistance, and thermal filling [1, 19-25]. Some of these ceramic composites have a super bond matrix with ordinary functional coating particulate such as Ni-ZrO₂, Al-SiC, Ni-PZT, Ni-Al₂O₃, Cu-Al₂O₃,

Additives of organic nature, surfactant and nano composite play an essential role in bright bath formulation for electrodeposition. According to [24-28] various organic compounds have been proposed and used as additives for zinc binary coating and extensively studied to obtain durable, uniform, and compact zinc coatings for corrosion prevention of steel products. Additives especially surfactant have been attested by [26-27] to provide organic molecules or minerals to the electroplating bath solution to exert crucial influences on the qualities and corrosion characteristics of the electrodeposits.

The present work reports results on the composition, chemical induction, properties, structure of electrodeposited Zn-Al₂O₃ alloy deposits obtained from an alkaline chloride bath containing TEA and MEA as essential surface-active additive agents. The produced coatings were characterized by Atomic Force Microscope (AFM), X-ray diffractometer (XRD) and scanning electron microscope (SEM) attached with energy dispersive spectroscopy (EDS). Micro-hardness was evaluated by a diamond-based DuraScan micro hardness test machine.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of substrate

Mild steel specimens of (40 mm x 20 mm x 1 mm) sheet were used as substrate and zinc sheets (60 mm x 30 mm x 2 mm) were prepared as anodes. The working mild steel specimens have a weight composition as described in Table 1. The cathode was mild steel coupons and anode was pure zinc (99.99%). The mild steel specimens were polished mechanically, degreased and immediately water washed following the study made by¹⁰.

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

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 activated 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-Al₂O₃ particles electrolytic solution as indicated in table 2. The formulations were then heated to 40°C to easy admix and dissolution of any agglomerate in the bath solution. The bath produced is concurrently stirred as heating trend lasted for hours before plating.

Table 2. Bath composition of Zn-Al₂O₃ alloy co-deposition in the presence of Tea and Mea

Composition	Mass concentration (g/L)
ZnCl	100
KCl	50
Boric Acid	10
Glycine	10
Al ₂ O ₃	10
Tea	2ml
Mea	2ml
pH	4.8
Voltage	0.5-0.8V
Time	10-15 min.
Tempt	40°C

2.3. Preparation of the coatings

Table 3. Formulated bath composition of Zn-Al₂O in the presence of Tea/Mea

Sample Order	Material sample	Time of deposition (min)	Potential (V)	Current/D (A/cm ²)
Blank	-	-	-	-
Sample 1	Zn-Al ₂ O ₃ +Tea/Mea	10	0.5	2
Sample 2	Zn-Al ₂ O ₃ +Tea/Mea	10	0.8	2
Sample 3	Zn-Al ₂ O ₃ +Tea/Mea	15	0.5	2
Sample 4	Zn-Al ₂ O ₃ +Tea/Mea	15	0.8	2

The prepared Zn-Al₂O₃ composite in the presence of Tea and Mea was heated for 2hrs and intermittent stirred to obtain clear solution before was prepared by electrolytic deposition process over mild steel. The prepared cathode and anodes were connected to the D.C. power supply through a rectifier at current density of 2 A/cm². Deposition was carried out at varying applied voltage between 0.5-0.8 V for 10-15 minutes. The distance between the anode and the cathode and the immersion depth was kept constant. Thereafter, the samples were rinsed in water and dry.

2.4. Structural Characterization of the coatings

The structural studies and elemental analysis of the plated samples were verified using a TESCAN scanning electron microscope with an attached energy dispersive spectrometer (SEM/EDS). Phase composition studies was carried out using PhilipsPW1713X-ray diffractometer (XRD) fitted with monochromatic Cu K α radiation set at 40kV and 20mA, while phase identification was done using Philips Analytical X' Pert High Scores software fitted with an in-built International Centre for Diffraction Data (ICSD) database. 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.

3. RESULTS AND DISCUSSION

3.1. Influence of Tea and Mea:

Course and dull deposit are produce from past work without surface-active compound [5]. Since, additive especially surface-active agents have proven to provide good adhesion strength and smaller grain adjustment. An attempt using Tea and Mea was aim to harness better surface nature and good crystal reaffirming of coating. Tea and Mea are used as active compound and neutraliser of acid component for corrosion prevention and emulsifiers [www.dou.com]. With 2 ml of each of addition agent, the nature of coating improved with bright and adorable deposit at 15 minutes, 0.8 V. Obviously, all coating perform excellent well in the presence Tea and Mea but the significant performance of the surfactant might be due to additive physiochemical characteristic.

3.2. SEM/EDS Surface Characterization of Deposited Sample

Figure 1 shows the scanning electron micrographs and attached EDs of the as-received mild steel substrate. Figure 2a-d display SEM/EDS of [a] Zn-Al₂O₃+Tea/Mea 10min at 0.5 V [b] Zn-Al₂O₃+Tea/Mea 10min at 0.8 V [c] Zn Al₂O₃+Tea/Mea 15min at 0.5 V [d] Zn-Al₂O₃+Tea/Mea 15min at 0.8 V. It is obvious that the whole plating show good surface modification, however, different surface structure were seen. The nature of the surface morphology and orientation in 2a unveiled larger crystal along the interface. This invariably implies that the porous nature observed are due to the interfacial stress between the particle and the metal matrix which could pave way for corrosive site.

With the deposits obtained in Fig. 2b a better structure compare to the formal were presented. A highly uniform dispersed of particulate and the enhanced surface active effects of TEA/MEA were seen to promote the compact site.

Although [3-4] stated that good surface morphologies in the presence of surface active agent promote preferential adsorption along major plans which could lead to preferential growth and less crystal size. Another significant reason for the behavior observed in Figure 2a and c might be as results of the deposition parameter. [4, 9] affirmed that the deposition behavior and the adhesion strength of any particular plating often based on the potential, current density and the most especially the time of deposition.

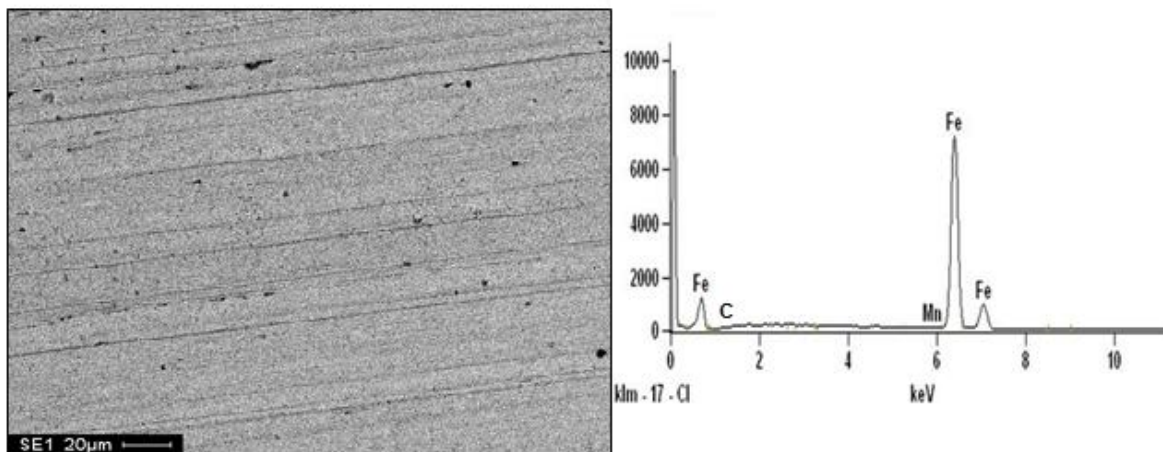


Figure 1. SEM/EDS micrographs of as-received sample

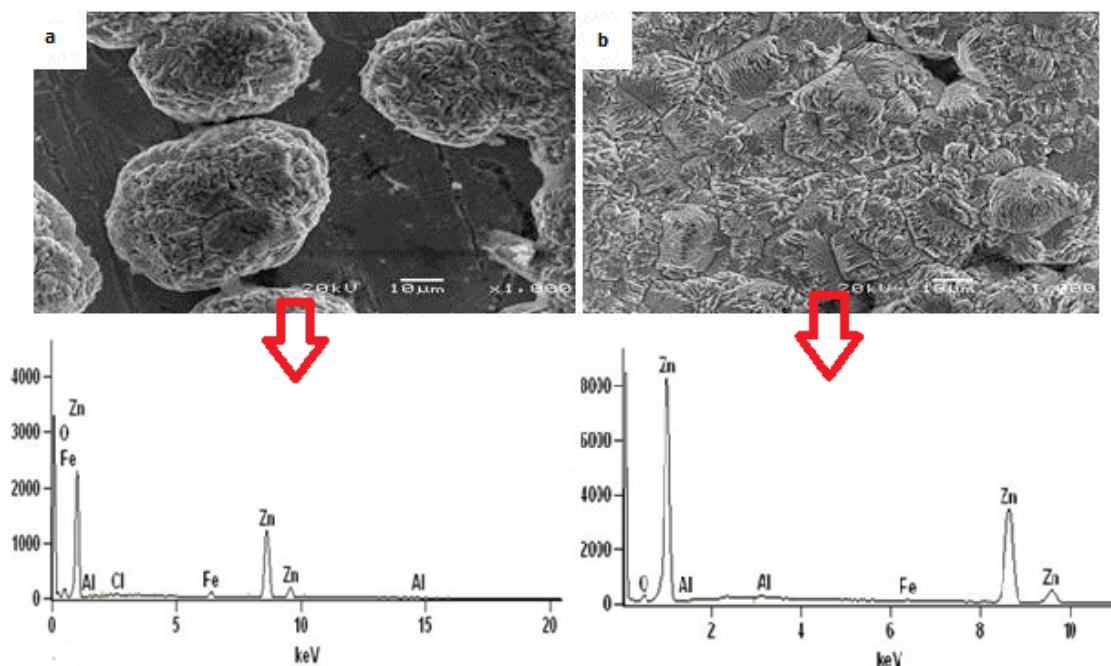


Figure 2. SEM micrographs of [a] Zn-Al₂O₃+Tea/Mea 10min at 0.5 V [b] Zn-Al₂O₃+Tea/Mea 10min at 0.8 V -X1000 magnification

The mechanism of co-deposition of alumina and surface-active agents on the zinc crystal could be generally seen to be influenced by the deposition rate and time. At (0.5V, 10minutes) those deposit produce show distinctive separation inform of agglomeration at the interface with the crystal in block formation. Figure 2b and 2d are surface morphologies of fabricated (Zn-Al₂O₃+Tea/Mea 10min at 0.8 V and Zn-Al₂O₃+Tea/Mea 15min at 0.8 V). It is apparent to see that TEA/MEA, deposition potential and time does not only enhance the deposition of the coating but revealing a significant levelling and brightening effects of the co-deposits with fine compactable and adhered shape observed.

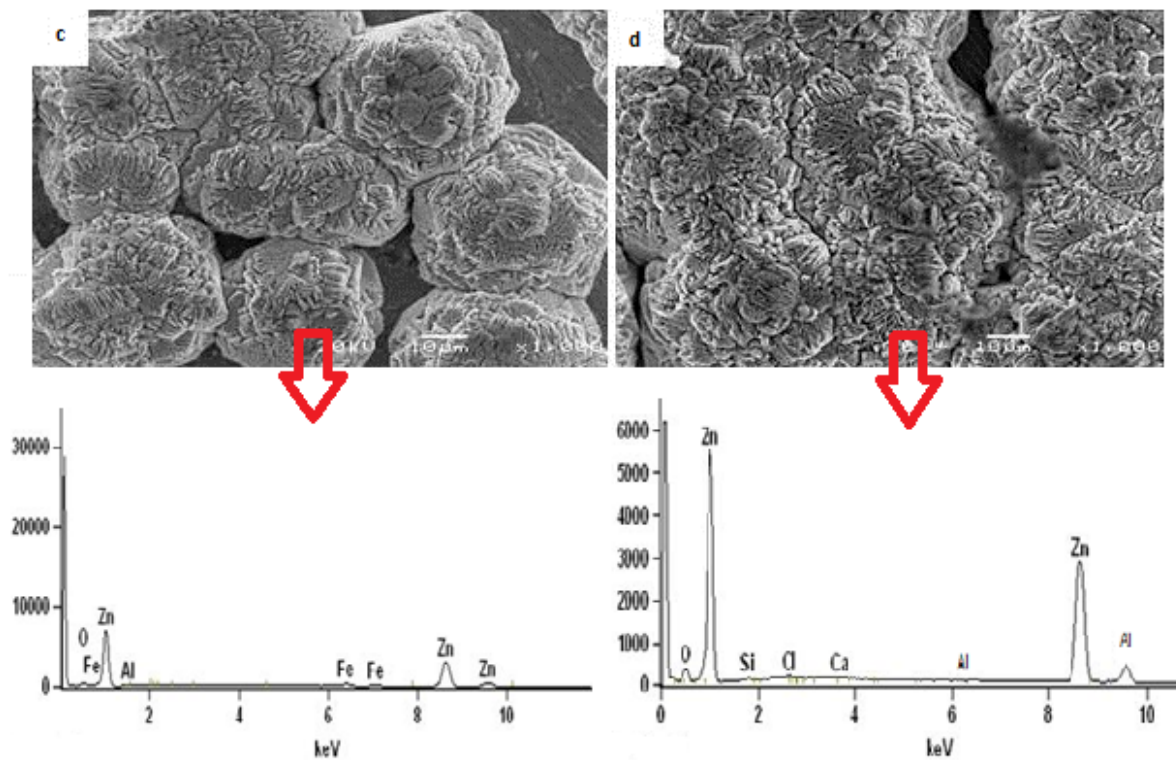


Figure 2. SEM/EDS micrographs [c] Zn-Al₂O₃+Tea/Mea 15min at 0.5 V [d] Zn-Al₂O₃+Tea/Mea 15min at 0.8 V -X1000 magnification

The AFM performed on obtained binary fabricated Zn-Al₂O₃ composite alloy at 0.5 and 0.8V, with varied time of deposition were illustrated in Fig 3.

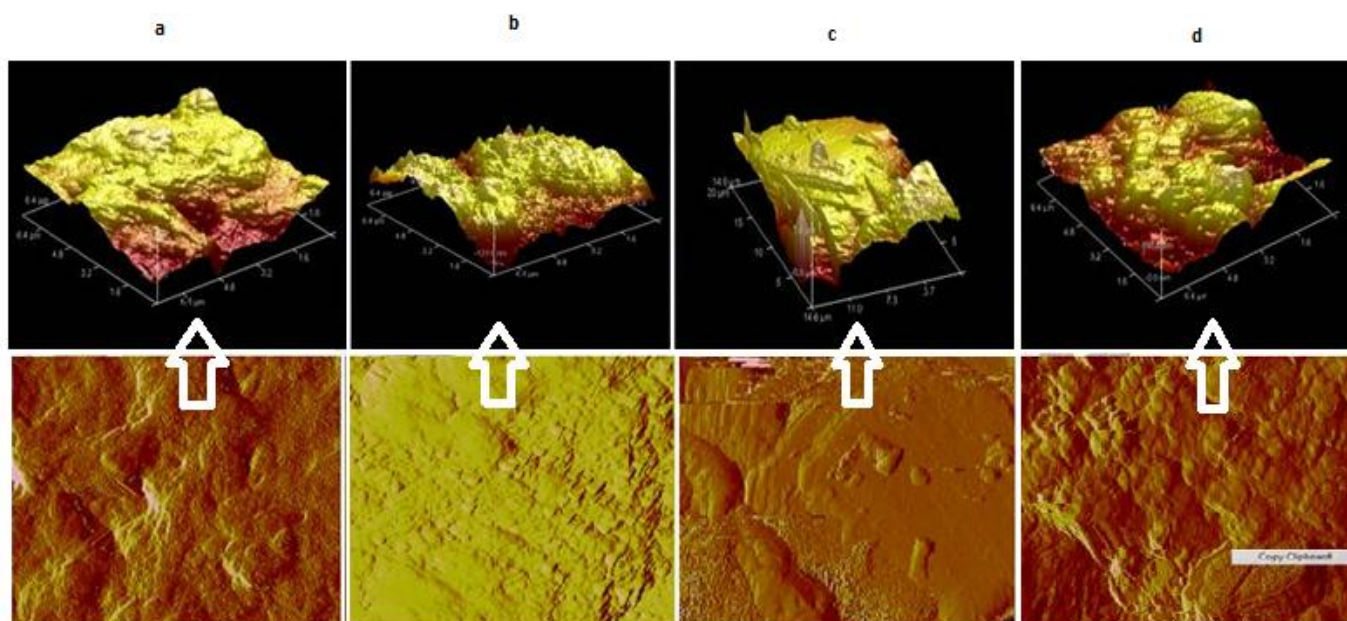


Figure 3: AFM micrographs of [a] Zn-Al₂O₃+Tea/Mea 10min at 0.5 V [b] Zn-Al₂O₃+Tea/Mea 10min at 0.8V [c]Zn-Al₂O₃+Tea/Mea 15min at 0.5V [d] Zn-Al₂O₃+Tea/Mea 15min at 0.8 V.

The general structure and topography of the alloy under the influence of different process parameter and surface-active agent shows uniform crystallites coalesced with small grain especially with deposit at 0.8V affirming the morphological result obtained from scanning electron micrograph. Good topological build-up was seen with the topography of Zn-Al₂O₃+Tea/Mea 15min at 0.8 V as against other coated alloy.

3.3. XRD phase evaluation

Fig. 4-5 shows the x-ray diffraction spectra of coated sample with various phases formed. Although good intensities were obtained from the examine coatings, which is an indication of good intermetallic and interfacial solid growth. The larger peak formed were observed within Bragg angle of 20° to 50°. Phase evolution such as Zn₂Al₂, ZnAl, Zn₃Al₂ and Zn₂AlO besides original Zn based particulate was observed within coating interface. Strong peak noticeable for produced alloy of Zn-Al₂O₃+Tea/Mea 15min at 0.8 V (Fig. 5) suggest a smooth interference and positive metal interaction with surface-active admixed. It is noteworthy to note that the interaction between Zn and Al₂O₃ and the levelers ultimately produces a good crystal orientation and phase seen rather than chemical dissolution of Al in the admixed formation. Hence, the surface structure of the deposits modified in the presence of Al₂O₃ and the surfactant are of extreme influence in this study since grains of the deposits is of importance as the electro-crystallization of zinc with other admix is very sensitive to bath formulation [3]. All deposited sample provide a good reflection of surface structure expected within the phase.

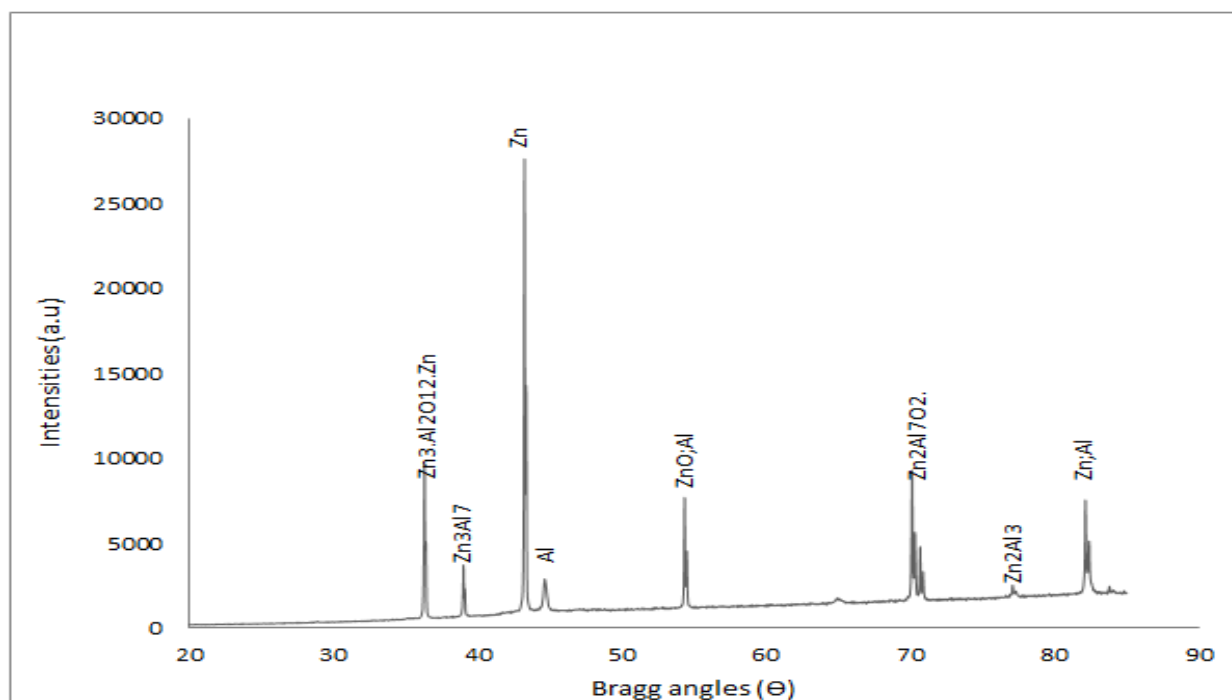


Figure 4. XRD Spectral of Zn-Al₂O₃+Tea/Mea in 10 minutes at 0.8 V

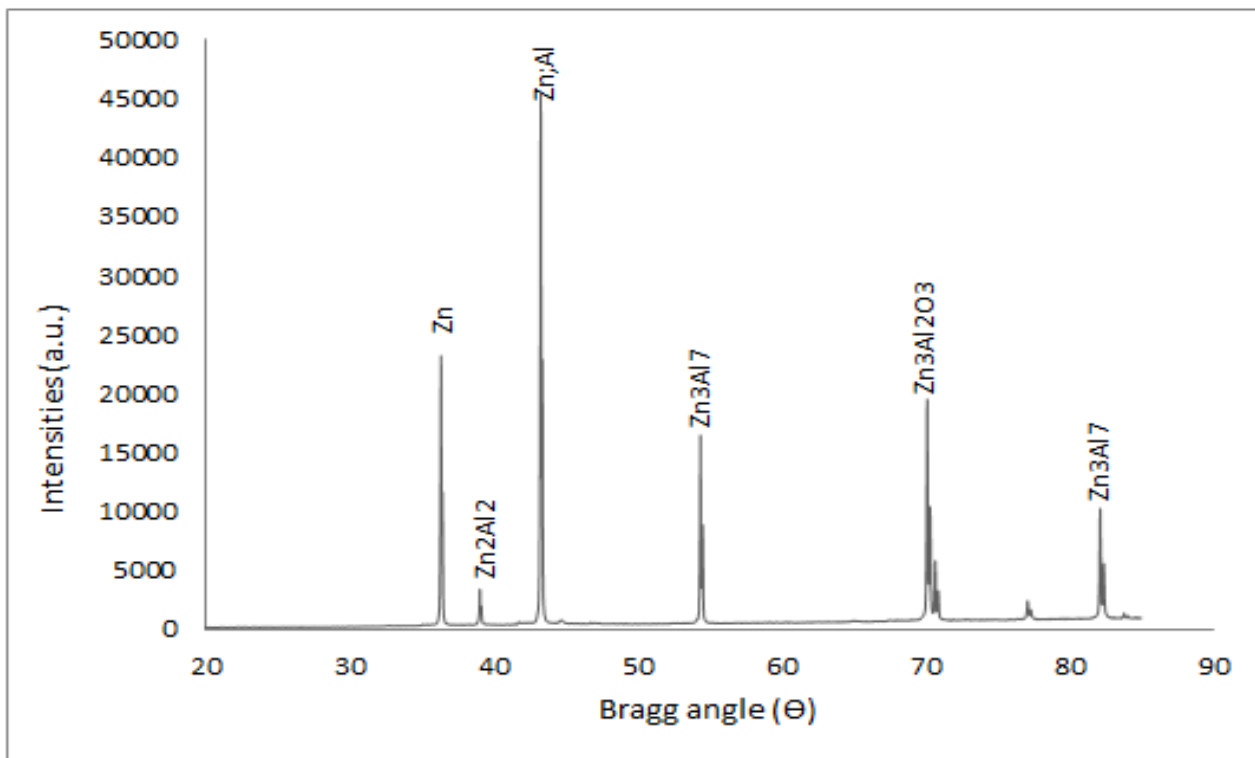


Figure 5. XRD Spectral of Zn-Al₂O₃+Tea/Mea in 15 minutes at 0.8 V

3.4. Micro-hardness studies:

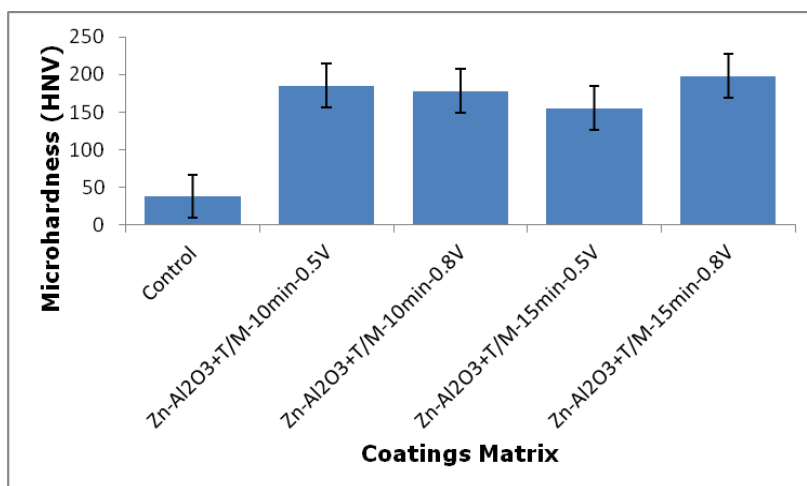


Figure 6: Variation of micro-hardness of composite fabricated coating at different process parameter.

Fig. 6 Present the effects of Al₂O₃+TEA/MEA at different applied voltage of 0.5 and 0.8 V in 10-15minutes with Zn metal interface on mild steel substrate. From all indications, the micro-hardness rise with additive dispersed into the bath. The pronounce micro-hardness change was noticed with Zn-Al₂O₃-TEA/MEA-15min at 0.8V. Although, all sample fabricated revealed outstanding hardness behaviour with the help of Al₂O₃-TEA/MEA strengthening effect in zinc matrix. Report from literatures by [7-10] show ceramics composite particles can lead to refinement in grain structure and

improve the micro-hardness of the composite coatings. [3, 27-28] also affirmed surface active agent adsorbed at the electrode surface thereby blocking further deposition and demising deposition rate. In view of this, the higher potential used help to restrain quick blocking of active site by TEA/MEA and promote levelling tendency for good crystal build-up which essentially contribute to the hardness properties seen. In order word the co-existence of surface-active compound with composite matrix in zinc blend could be seen to contribute to build-up and hence promote nonexistence of cracks and flaw.

4. CONCLUSION

✚ In this work, mixed Zn-Al₂O₃ in the presence of surface-active additive Tea and Mea films by electrolytic co-deposition technique have been deposited on mild steel substrates successfully

✚ The surface modification was found to be significantly dependent on the particle incorporation and the vol. ration of surface-active agent.

✚ Intermetallic phases such as Zn₂Al₂, ZnAl, Zn₃Al₂ and Zn₂AlO were seen to contribute immensely to the buildup of strong adhesion found from the coating.

✚ In general, from the morphological, mechanical and electrochemical studies, Zn-Al₂O₃+Tea/Mea 15min at 0.8 V alloy coating have shown better performance than others in their homogeneous diffusion and interfacial trend.

✚ Improved mechanical resistance performance was obtained from the deposits as against the as-received substrate.

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