
Experimental study and sustainable surface-active effect of ECA hybrid particulate on tin-zinc infringement coating developed via DAECD technique on AISI 1015 steel

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Abstract: The effect of sustainable degradable eco-friendly extract juice on the precipitation and re-enforcement of Zn-SnO₂ alloy matrix with the aim of producing an eco-friendly composite material for engineering structural applications was investigated. Composite samples were produced from these mixtures and the effect of coconut juice (5–15% concentration) on the microstructure evolution, the mechanical properties of the composites and electrochemical behaviour were investigated. Scanning electron microscope

(SEM-EDS) and atomic force microscope (AFM) were used to study the surface morphology and the surface adherent properties of the coatings. Micro-hardness behaviours were investigated by means of high impact diamond Dura scan microhardness tester. The result shows that Zn-SnO₂-15CJ sulphate co-deposition contributed to increase hardness than Zn-SnO₂ alloy. It was observed that Zn-Zn-SnO₂-15CJ sulphate has excellent corrosion progression at ambient temperature. The hardness performance shows that developed Zn-SnO₂-15CJ is increased by 80% compared to as received sample and 25% compared to Zn-SnO₂.

Keywords: sustainable extract; composite; re-enforcement; X-ray diffraction spectrometer; XRD; microstructure.

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1 Introduction

Excellent mechanical properties of mild steel properties make it remain the most widely used material for both domestic and industrial application (Anawe et al., 2017a; Fayomi and Popoola, 2012; Popoola and Fayomi, 2011; Popoola et al., 2012). The massive use of mild steel in structural and engineering applications is due to its availability, low cost and

physical properties (Popoola et al., 2012). Hence, it has restricted application which is intensively caused by the interactions between external environments. The above-mentioned challenge range from chemical and mechanical interaction depending on the service area.

Due to these disadvantages, many protection methods have been embraced to improve the service life of mild steel against corrosion and wear attacks. Among these, electro-deposition method with metallic thin films of various interests has been worked upon (Xiaosong et al., 2012). The stability of the fabricated coatings and their surface behaviour establishes further development of these coatings for acidic and alkali environment applications (Radojcic et al., 2008). Electro-deposition of Zn produce thinner coating with less protection as compared to Zn composite coating that is suitable for the subsequent forming process in the automotive industries (Grozdananov et al., 2006).

Many researchers have investigated on the use of natural eco-friendly additives in electrodeposition bath and how they affect the chemical and mechanical properties of the low carbon steel substrate (Yang et al., 2004). The use of solanum tuberosum and saccharum officinarum as reinforcement has been studied by Rifagat et al. (2012) and Fayomi et al. (2017) in attempt to better the morphology of the electrodeposited coatings. The results showed that the mechanical and electrochemical properties of the coating with eco-friendly additives improved significantly. It is also reported by Kanyane et al. (2016) and Fayomi et al. (2011) that eco friendly additives causes changes in structural evolution which provide restriction over possible dislocations and failure. This is apart from the cost incur and availability (Suantak et al., 2011).

Loto et al. (2012) also studied the effect of sugar cane as additive agents in the electrodeposition of zinc from acid-based solution. A fairly good zinc electrodeposition on mild steel substrate was obtained in the acid zinc chloride solution. Surface active activities of the particulate were seen to provide a preferred coating but regrettably the phase change and mechanical effect of the coating was not reported. In this study, coconut juice (CJ) as eco-friendly reinforce materials was added to Zn-SnO₂ electrodeposition bath to boast the physical, mechanical and electrochemical properties of the developed coating. An attempt will also be made to investigate the impact of the process parameter on the stable crystal stability of the Zn-SnO₂ developed coating.

2 Methodology

2.1 Preparation of substrate

Mild steel specimens of (40 mm × 20 mm × 1 mm) sheet were used as substrate and zinc sheets (60 mm × 30 mm × 2 mm) were prepared as anodes. The working mild steel specimens have a weight composition as described in Table 1. The cathode used is mild steel coupons and anode was pure zinc of (99.99%). The mild steel specimens were polished mechanically using different grades of emery paper in the order of 60, 120, 400, 800 and 1,600 μm to erase any existing surface impurities and tracks. The samples are further degreased and immediately water washed as par required standard mentioned by Anawe and Fayomi (2017a).

Table 1 Spectrochemical composition of mild steel

<i>Element</i>	<i>C</i>	<i>Mn</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Al</i>	<i>Ni</i>	<i>Fe</i>
(%) 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 five seconds followed by rinsing in distilled water. Analytical grade chemicals and distilled water were used to prepare the plating solution at room temperature. Prior to plating, the CJ was added to the prepared Zn-SnO₂ alloy 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 three hours before plating. The design framework is presented in Table 3.

Table 2 Bath composition of Zn-SnO₂-CJ frame work in the presence of CJ

<i>Composition</i>	<i>Mass concentration (g/L)</i>
ZnSO ₄	100
SnO ₂	15
NaSO ₄	35
CJ	5g–15
Boric acid	10
Glycine	10
Parameters	
pH	4.6
Time	10 min
Current density	1.0 A

2.3 Structural characterisation

The structural studies and elemental analysis of the plated samples were verified using a TESCAN scanning electron microscope coupled with energy dispersive X-ray analyser (SEM/EDS) and an optical microscope (OPM). EDX analysis was used to observe the elemental composition. The adhesion profile, topography and morphology of samples surface before and after coating was observed with the help of atomic force microscope (AFM).

Table 3 Summarised data of Zn-SnO₂/CJ of electroplated samples

<i>Sample order</i>	<i>Time of deposition (min)</i>	<i>Current density (A/cm²)</i>
Control	-	-
Zn-SnO ₂	10	1.0
Zn-SnO ₂ -5CJ	10	1.0
Zn-SnO ₂ -15CJ	10	1.0

2.4 *Microhardness studies*

The harness characteristics of the electrodeposited samples and as-received specimens were determined by the use of emco micro-hardness tester with a dura scan diamond indenter. Indentations were made across the deposited layer at three locations using a load of 10 g for ten sec and the average mean hardness was used to obtain the final micro-hardness performance of the materials.

2.5 *Electrochemical studies*

A conventional three electrode cell consisting of saturated calomel (SCE), graphite, and coated mild steel as 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 potentiostat/Galvanostat with a fixed potential from -1.5 V to $+1.5$ mV with scan rate of 0.012 V/s.

3 **Results and discussion**

3.1 *SEM/EDS surface characterisation of deposited sample*

Figures 1(a) and 1(b) show the scanning electron micrographs (SEM) and attached EDS of the deposited samples containing Zn-SnO₂ and Zn-SnO₂-15CJ respectively. From deposition appearance of all fabricated samples, they display better morphology and good adhesion. The nature of the surface morphology and orientation in Figure 1(a) unveiled the homogeneous appearance with good discharges as expected. One significant reason for this behaviour might be as results of the deposition parameter and the presence of SnO₂ (Amuda et al., 2009; Oluwole et al., 2009). Fayomi et al. (Oluwole et al., 2009) confirmed that the deposition behaviour and the adhesion strength of any electrodeposited coatings are often based on the potential, current density and the most especially the time of deposition. The addition of CJ as natural additive resulted in non-homogenous structures with pores [see Figure 1(b)]. These findings contradict the studies of Kanyane et al. (2016) and Anawe and Fayomi (2017a) were the author's ascertained that addition of natural additives results in better and uniform morphology. Coconut additives resulted in complete opposite of the studies of the mentioned authors. In all, the fabricated appearance of the coatings shows preferred adhesion and stable deposit. The energy dispersion spectrum (EDS) was engaged to draw conclusions on the elemental composition of the deposited coatings [Figures 1(a) and 1(b)]. There is clear validation between the EDS of the fabricated coatings with and without CJ on zinc-based matrix results. Both Zn-SnO₂-CJ and Zn-SnO₂ showed Zn, SnO₂, O and Si peaks.

Figure 1 SEM/EDS of (a) Zn-SnO₂ and (b) Zn-SnO₂-15CJ 10 min at 1.0 A (see online version for colours)

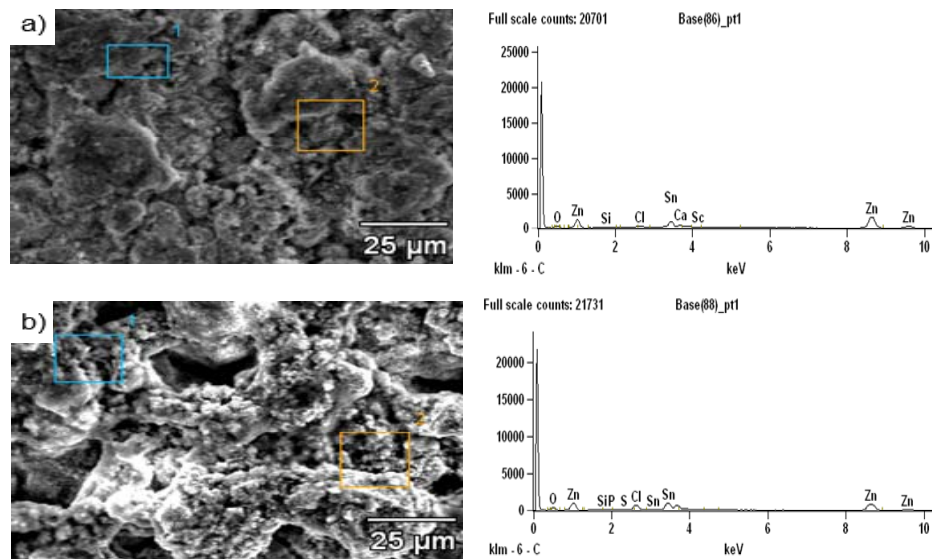
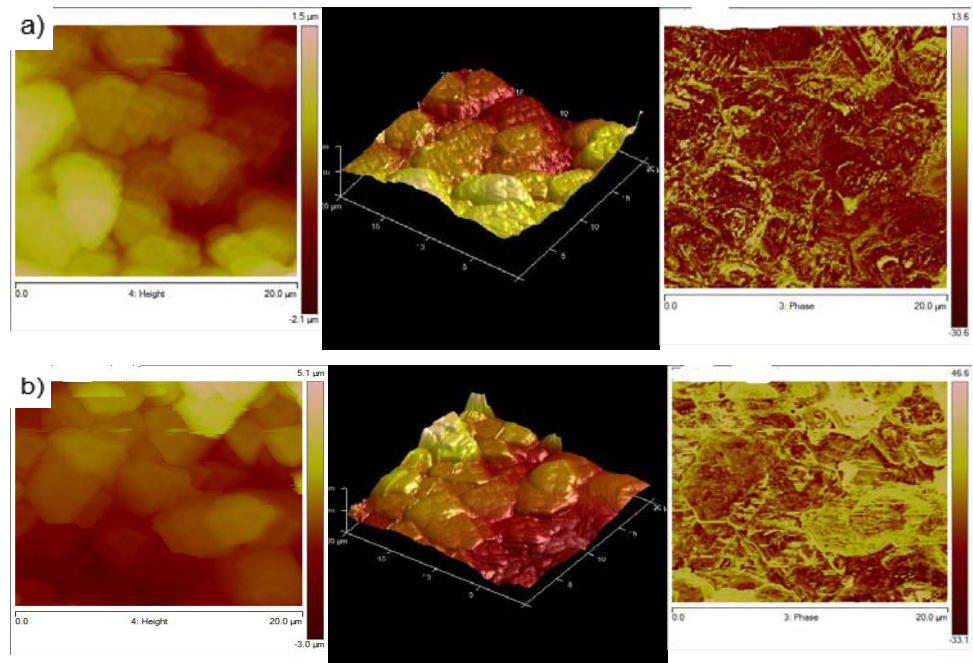


Figure 2 AFM micrographs of (a) Zn-SnO₂ and (b) Zn-SnO₂-5CJ (see online version for colours)



3.2 AFM analysis

The coating roughness and topography of Zn-SnO₂ and Zn-SnO₂/CJ obtained at current of 1.0 A and deposition time of ten min with the help of AFM are shown in Figure 2. In all fabricated coating, uniform crystallites and even roughness was seen in Figure 2(a) with Zn-SnO₂. The result is in trend with morphological result obtained from scanning electron micrograph.

The topography of the Zn-SnO₂-CJ matrix show better adhesion behaviour with spherical, flat and hexagonal platelets deposition which indicates coconut dispatches. The growth of spherical crystallites does not cover the entire surface, thereby giving it a non-uniform appearance (Anawe et al., 2017c; Vathsala and Venkatesha, 2011). However finer grain texture and dendrites free deposition were obtained and observed in all AFM images.

3.3 X-ray diffraction spectrometer (XRD) phase evaluation

Figures 3(a) and 3(b) shows XRD spectral of Zn-SnO₂ and Zn-SnO₂-15CJ respectively. The XRD analysis provides detailed information on the crystallographic structure and physical properties of the deposited thin films. From the phase identification a strong peak was noticed with Sn and Zn interface as major constituent. The presence of this constituent has been reported by Amuda et al. (2009) to provide high strength composite matrix. The interaction between Zn and SnO₂ ultimately produces a crystal orientation of grain size rather than chemical dissolution of Sn in the admixed formation (Fustes et al., 2008). More so, the improvement of different crystal phases can be related to the growth of grains owing to its compactness. It is good to mention that the surface structure of the deposits in the presence of SnO₂ and the surfactant are of remarkable influence in this study since grains of the deposits is of importance as the electro-crystallisation of zinc with other admix is very sensitive to bath formulation (Anawe et al., 2017b). All deposited sample provide a good reflection of surface phase Zn₂OSn₂, ZnOSn₂ and ZnSn which is expected within the lattices.

Figure 3 XRD spectral of (a) Zn-SnO₂ and (b) Zn-SnO₂-15CJ (see online version for colours)

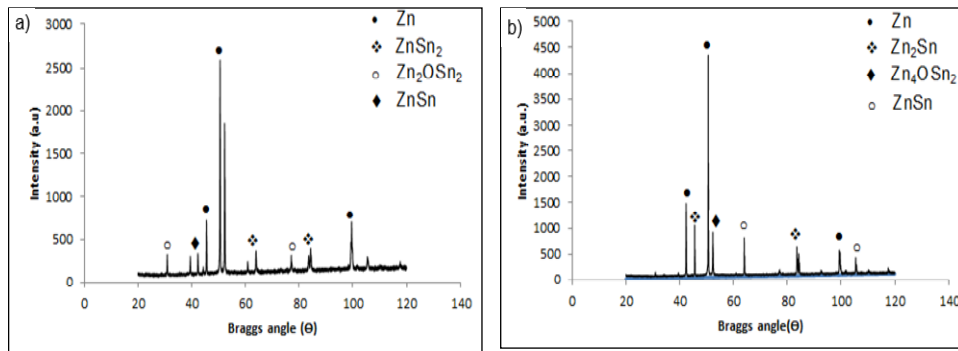
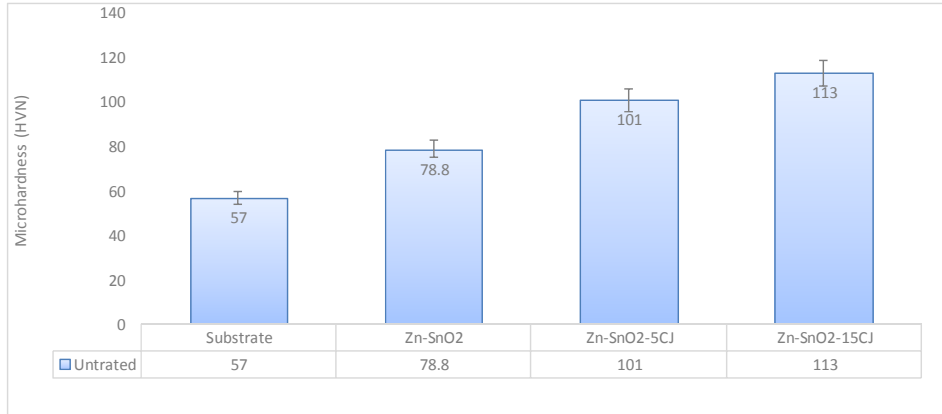


Figure 4 present the effect of CJ on the mechanical properties of Zn-SnO₂ coatings. A noticeable microhardness change with all sample matrixes with respect to CJ content were seen with CJ strengthening effect. Report from literatures by Bobić et al. (2010) and Batzill and Diebold (2005) showed that ceramic composite particles can lead to refinement in grain structure and hence improved the microhardness characteristics of the

composite coatings. In other word, composite-CJ thus changes and cause stable grain and provide structural modification which could enhance the hardness performance. The produced phases confirmed by the diffraction plays important role in the increase in microhardness properties which is par with study by Anawe and Fayomi (2017b).

Figure 4 Variation of microhardness properties of Zn-SnO₂ and Zn-SnO₂-CJ coatings (see online version for colours)



3.4 Electrochemical studies

The behaviour of the fabricated coatings on AISI 1050 steel to corrode in 3.65% NaCl was examined and presented in Figures 5 and 6. The result from the polarisation resistance (Ω) and corrosion rate (mm/yr) progression show that there is an increase in polarisation resistance with the addition of CJ on Zn-SnO₂ alloy. Mild steel possesses the lowest polarisation resistance of 27.6 Ω . The highest polarisation (R_p) of 171 Ω was attained for Zn-SnO₂-CJ with 140.3 Ω for Zn-SnO₂ among the coating succession. It is worth mentioning that the coating on 15CJ had substantial improvement as against the 5CJ coating.

Figure 5 Polarisation resistance trend (Ω) of various coated alloys in 3.65% NaCl concentration at 25°C (see online version for colours)

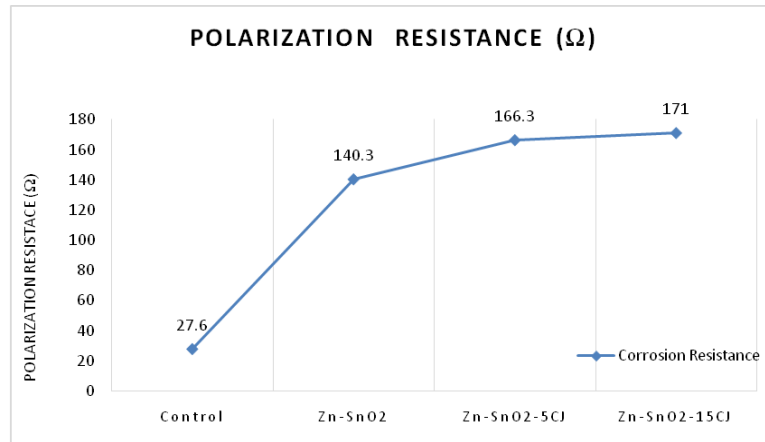
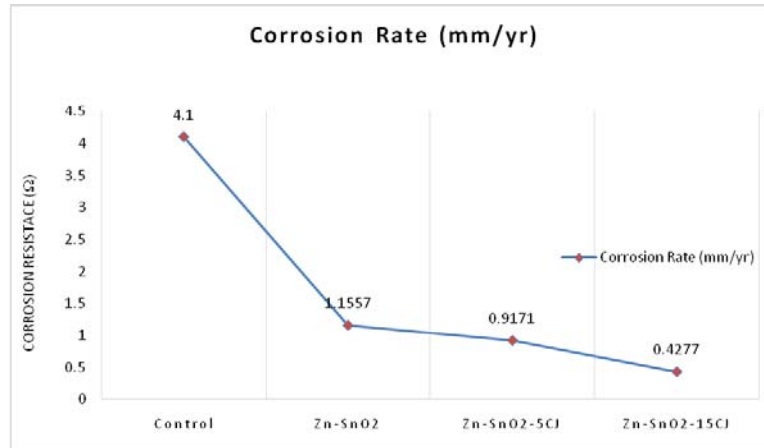


Figure 6 Corrosion rate trend of various samples in 3.65% NaCl at 25°C (see online version for colours)

From Figure 6, it is observed that the corrosion rate in (mm/year) of the fabricated coatings follow similar tendency as polarisation resistance in the reverse order. The decrease in corrosion rate as compared to control sample is accredited to the good interfacial bonding of the composites coatings on the substrate. The addition of CJ decreases the corrosion dissemination significantly as compare to other coating without natural additives. An increase in CJ also resulted in decreased corrosion rate. Corrosion rate of 0.1557 mm/year, 0.9171 mm/year and 0.4277 mm/year were obtained for the Zn-SnO₂, Zn-SnO₂-5CJ and Zn-SnO₂-15CJ respectively. For the as-received steel the corrosion rate of 3.2 mm/yr was attained showing a massive degradation as a result of non-protective coating.

4 Conclusions

- SEM and XRD analysis revealed the presence of the SnO₂ particles in the fabricated coatings and its crystallographic orientation on Zn matrix.
- Zn-15SnO₂-15 coconut showed better corrosion resistance as compared to the rest of the deposited coatings.
- The electrodeposition of Zn-SnO₂-CJ samples are capable of protecting mild steel in chloride medium to retard corrosion attack.
- The addition of CJ as natural additive into electrolytic Zn-SnO₂ bath brought about enhanced structural evolution. The hardness of the fabricated coatings increased to 113 HVN as compared to 57 HVN of AISI 1015 steel.

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