Electro-Oxidation Performance and Photo-Structural Characterization of Induced Natural Additive on Chloride Electrolyte Thin film Coated Steel

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(Received on 11th March 2013, accepted in revised form 19th September 2013)

Summary: Improvement of engineering materials to avert corrosion, toxicity and to enhance the appealing value of steel has led to an enlarged interest in electro-deposition industries. The effect of solanum tuberosum (ST) extracted juice and Al dispersed particulate for Zn bath electrodeposition on mild steel from aqueous chloride solutions was investigated. The electrodeposition was carried out by adding Al particles and ST to a zinc-containing bath. Corrosion tests were performed at room temperature in 3.65 mol dm^{-3} NaCl solutions by cyclic potentiodynamic and open circuit polarization. Characterizations of the electrodeposited coatings were carried out using scanning electron microscopy equipped with energy dispersive spectrometer (SEM/EDS) and X-ray analysis diffraction (XRD). The experimental results show that significant change in the presence of the additives influences the crystal orientations, resulting into precipitation of $ZnAl_3$.Si and Zn_2Al_5 phases. The change in structure can also be linked to a robust blocking effect of the cationic surfactant of solanum tuberosum juice and Al dispatched oxide films which might influence nuclei replenishment and impact smaller grain size.

Keywords: Solanum tuberosum, Microstructure, Interface, Enhancement, Deposition.

Introduction

The excellent properties of mild steel among metal and alloy cannot be over emphasized. But it vulnerability to corrosion attacks is extensively high. Major effort by researchers in the area of surface engineering especially through electro-deposition has continued to grow to restrain the destructive effects of corrosion using several preventive measures [1-5]. Among the efforts to improve the corrosion stability of pure zinc coatings have been directed towards alloying it with more noble metals such as nickel, cobalt, iron, and cadmium [6-14]. It is also found that the characteristics of the deposited coating depend on the process parameters [6, 15-19]. The microstructure of the surface of the electrodeposited Zn alloy is another essential property which controls the corrosion resistance and other mechanical behavior [6, 18, 20-24].

One major setback of the electrodeposition process is the generation of internal microcracks. Hence, the stress propagation can be minimized by addition of natural juice extract inhibitors/additive and pure dispersed particulate in the bath condition [25-34]. [9] codeposited veratraldehyde (VRTD) in the Zn-Ni matrix and reported that the incorporation increased the brightness and the morphology of the coated surface. [29-34] studied the effect of organic additive on the mechanical and corrosion behavior of Zn electrodeposition using sugarcane and cassava juice extract on mild steel. The inclusion of natural juice extracts reduced stress formation and impact stability on the surface morphology.

Some additives serve as wetters surfactants, which reduce surface tension while, brighteners provide desirable aesthetic value for the electroplated metal. Organic compounds have been discovered as brightening agents in electroplating. In addition to the discovery of these compounds as brighteners, investigation into the use of natural organic compounds as substitutes is being undertaken.

The interest in using natural organic compounds is because of its availability, cost and effect on the environment [31-34]. They pose no detrimental effect on the environment or hazard to human health. A number of natural organic compounds have been identified as good brightening agents in zinc electroplating. Examples of these substances are sugarcane extract, cassava juice extract [33-34]. More so, there is a gap in this research area, as few natural organic additives have been discovered. In this study, Al particles were dispersed and solanum tuberosum organic extract juice portion was added in Zn plating solution and a Zn-Al-ST coating was deposited on the steel substrate. The potentiodynamic polarization method was employ for corrosion stability test and

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morphological/phase using (SEM/EDS, XRD) were used to established the structural properties.

Results and Discussion

SEM/EDS Studies

Fig. 1a-c show the nature of crystal growth and orientation in presence and absence of additives as described with the help of SEM/EDS micrographs. Fig. 1a show the features of the as-received sample, Fig. 1b-c shows the SEM images of Zn coated sample and Zn- Al-ST coated sample respectively. Deposit obtained from Zn coating has coarse–grained deposit having non uniform crystal size. In presence of Al-ST (Fig. 1c) better grain size in the deposit was observed attesting to a modified crystal growth.

From structural observation, non-homogenous change in surface structure and roughness was seen in Fig. 1b. The difference in surface roughness (*R*a) may be as a function of coating time or additive exclusion [4-5, 24]. It is needful to say that the presence of additive particulates enhances the refinement of crystal size and regulates the uniform morphology of the crystals. More so [24] affirmed that surface roughness increased linearly with the increased coating thickness. Hence, thinner coatings exhibited lower surface roughness which is in agreement with the observation in this study in which the presence of additive not only improve surface morphology but also facilitate strong adhesion of the thin films over the substrate.

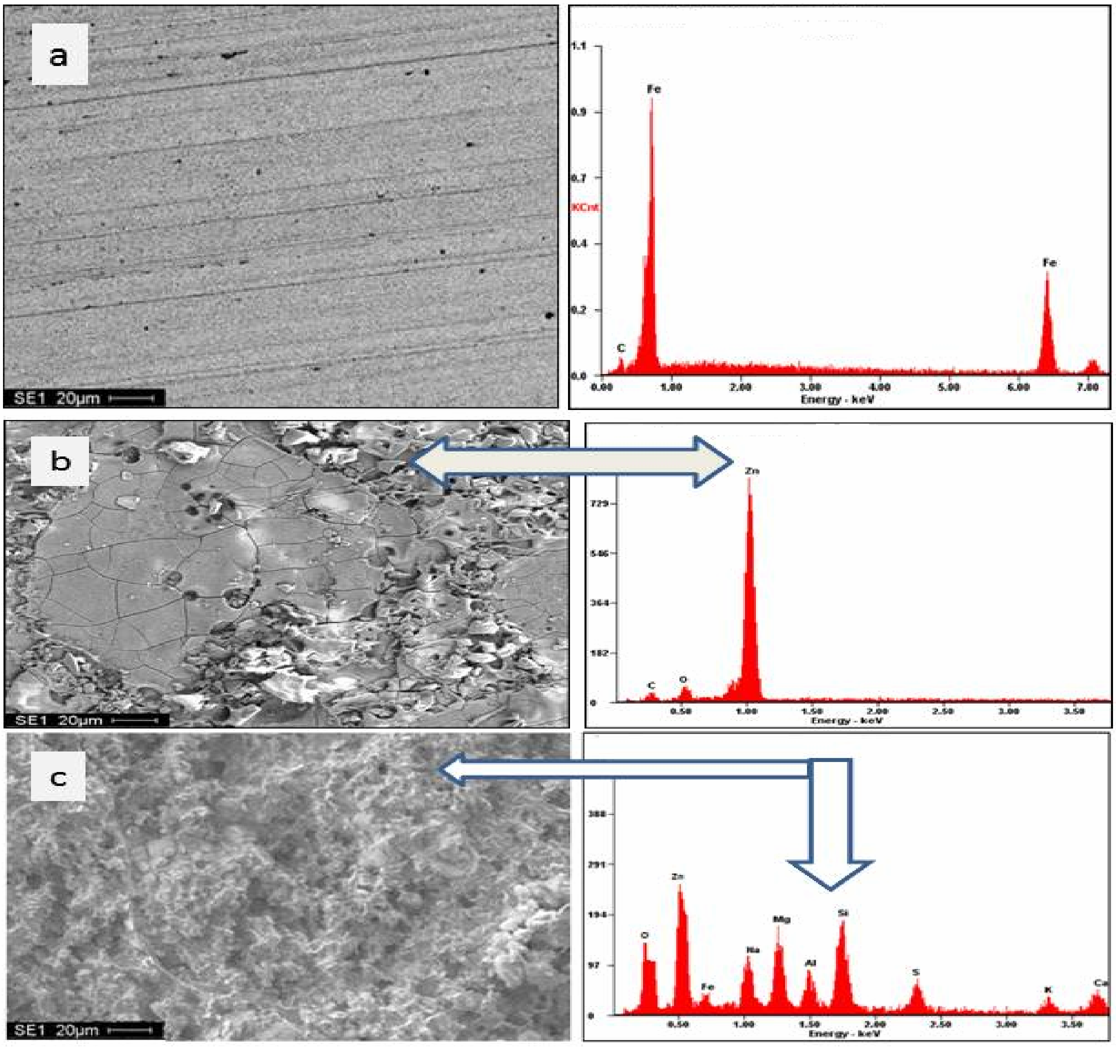


Fig. 1: SEM photomicrographs of a) the substrate surface b) Zn coating without addition agents c) Zn deposits in the presence of Al-ST addition agents.

It is apparent to say at this point that the change in structure can be linked to a robust blocking effect of the cationic surfactant of solanum tuberosum juice and Al oxide films in either case which might influence nuclei replenishment and hence impacting smaller grain size.

It is also significant to mention that the presence of the addition agent improves the bond strength during deposition which is also due to the adsorption of ST- group in the deposit sites. From this observation, we agree with [9, 28, 32] that adsorbed molecules have a significant influence on the steel surface coverage, and also the effect of surfactant caused a strong blocking effect leading to a smoother surface by nuclei renewal rate. No significant porosity defects observed rather a close surface structure and bright appearance, as obtained in Fig. 1c, It is also anticipated to provide significant corrosion resistance behavior since microstructure have a direct impact on coating properties [4-5]. The leveling and brightening influence of solanum tuberosum juice was excellent on the surface structure.

EDX analysis performed on the deposit obtained in presence of Al-ST revealed Zn, Al and other surfactant elements present which are the major constituents. The effect of Al particle size on deposition morphology and ST will help in major structural applications. Hence, reinforcing particles represented with juice extract in this work are desirable.

XRD Analysis

The XRD patterns of plated layers on steel are given in Fig. 2 and 3, respectively. In the XRD study performed for Zn–Al–ST coating, Zn, Zn-AlO, Zn_2Al_{13}.Sn, and ZnAl crystal phases were identified in the coating interface. While that of zinc depicted the presence Zn, ZnO, ZnO_2. The preferred crystal orientation with peak justifying electrodeposited Zn-Al-ST was observed. The formation of Zn_2Al_{13}.Sn phase content indicates that the precipitation will enhance the corrosion resistance of the alloy [29]. Therefore, these results revealed that the Zn–Al deposits obtained in presence of ST, unveiled higher corrosion resistance compare to the ordinary single phase zinc precipitation.

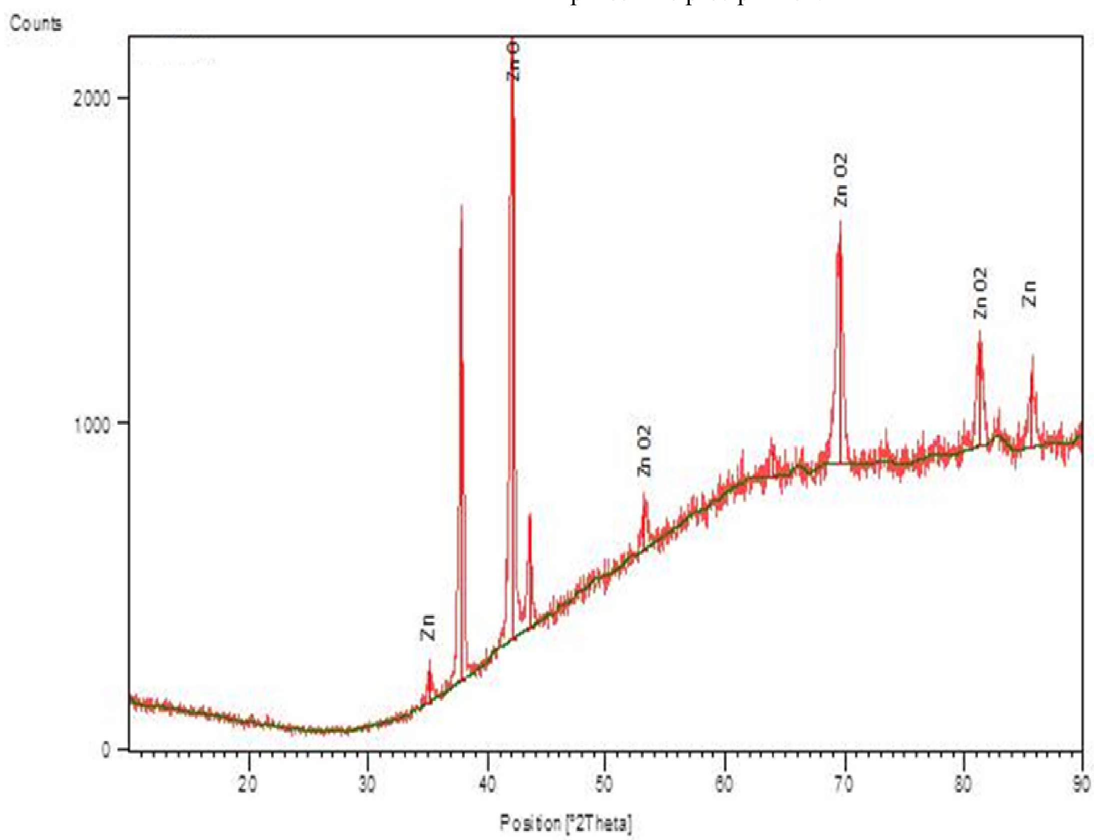


Fig. 2: XRD patterns of electrodeposited Zn alloy on steel from a chloride bath at 2 A/dm^3 for 20 min at 30^oC without Solanum tuberosum and Al dispersed

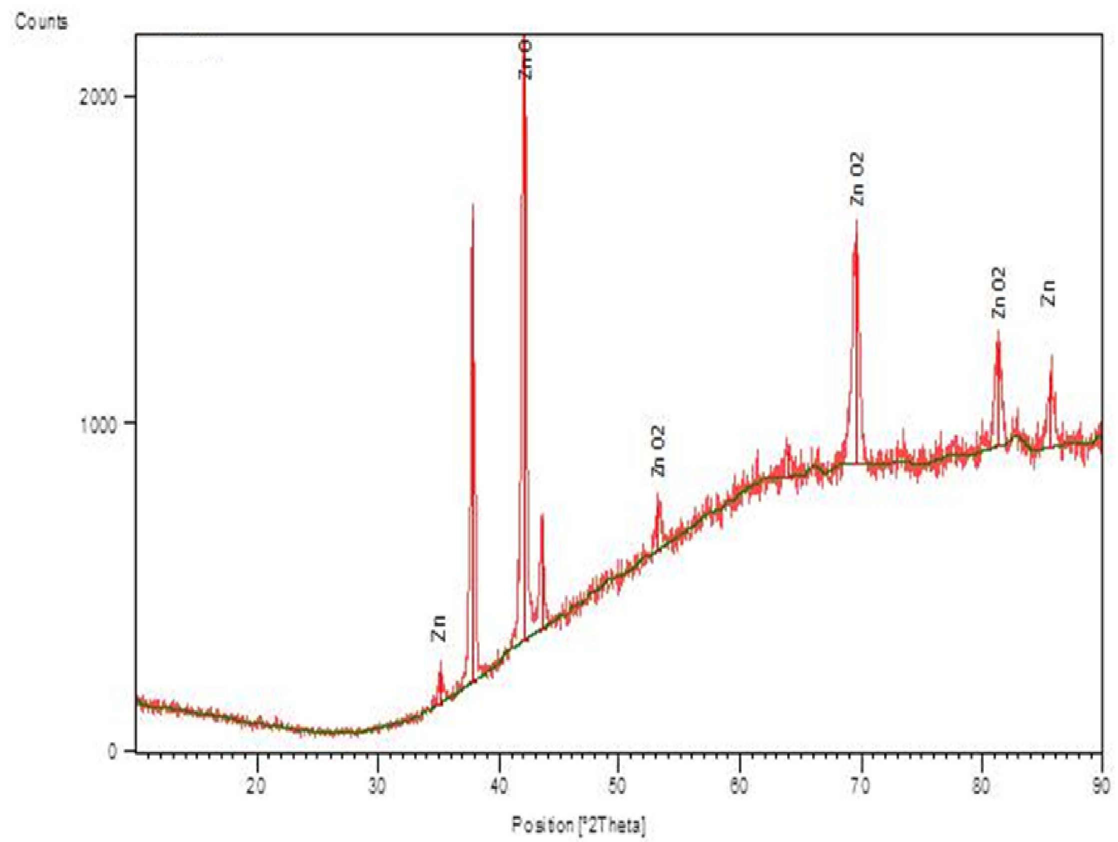


Fig. 3: RD patterns of electrodeposited Zn- incorporated Solanum tuberosum and Al on steel from a chloride bath at 2 A/dm^3 for 20 min at 30^{o}C

Electrochemical Test Result

The cyclic potentiodynamic polarization test was carried out in 3.65 % NaCl solution. The data of the potentiodynamic tests for Zn and Zn deposited Al-ST is showed in Table-1. It can be noticed that all induced deposited samples showed a passive behavior, with reduced current densities and better corrosion potentials. Considering Fig. 4a-c critically from the linear scan, the corrosion potential of the deposited sample; Zn (without Al-ST) was -0.800 V, Zn (with Al-ST) is -0.500 V, while that of mild steel is -0.910 V. These affirmed that, the corrosion rate mechanism with the co-deposited sample decrease with higher polarization resistance observed.

Table-1: Potentiodynamic polarization results.

Sample	i_{corr} (A)	I_{corr} (A/cm^2)	R_P (Ω)	E_{corr} (V)	Corrosion rate (mm/yr)
As-received	**1.04x10^{-1}**	**7.04x10^{-2}**	**2.76x10^2**	**-1.910**	**4.1x10^0**
Zn	**1.00x10^{-3}**	**1.5x10^{-4}**	**2.89x10^3**	**-0.800**	**8.3x10^{-2}**
Zn-Al-ST	**1.30x10^{-5}**	**2.5x10^{-6}**	**2.97x10^5**	**-0.500**	**6.4x10^{-5}**

At the reverse scan the behavior of the sample followed the same trend with Zn having potential of about -1.000 V, Zn (Al-ST) was -0.750 and the substrate with -1.110 V. In order words, deposited samples demonstrated passive phenomena at their region than the mild steel sample (Fig. 4). The value of corrosion current density, icorr, from the polarization curves shows a higher trend of corrosion current penetration. For mild steel, the icorr was about 1x10^{1}A/cm^2 Zn (without-Al-ST) was 1x10^{3}A/cm^2 Zn (with Al-ST) was 1x10^{4}A/cm^2. That means there is a positive mega shift of corrosion density of about 0.001 which is enough to justified response of the surface protection of the substrate.

From the open circuit polarization (OCP) studied employed to affirmed the interfacial and passivative mechanism, the effect of coating on the substrate were clearly seen in Fig. 5. The corrosion potential (Ecorr) for Zn change significantly in response to OCP time in the working electrolyte (see Fig. 5b) which means that the electrochemical behaviour of Zn coatings in 3.65% NaCl solution have an improve slot compare to the as received steel.

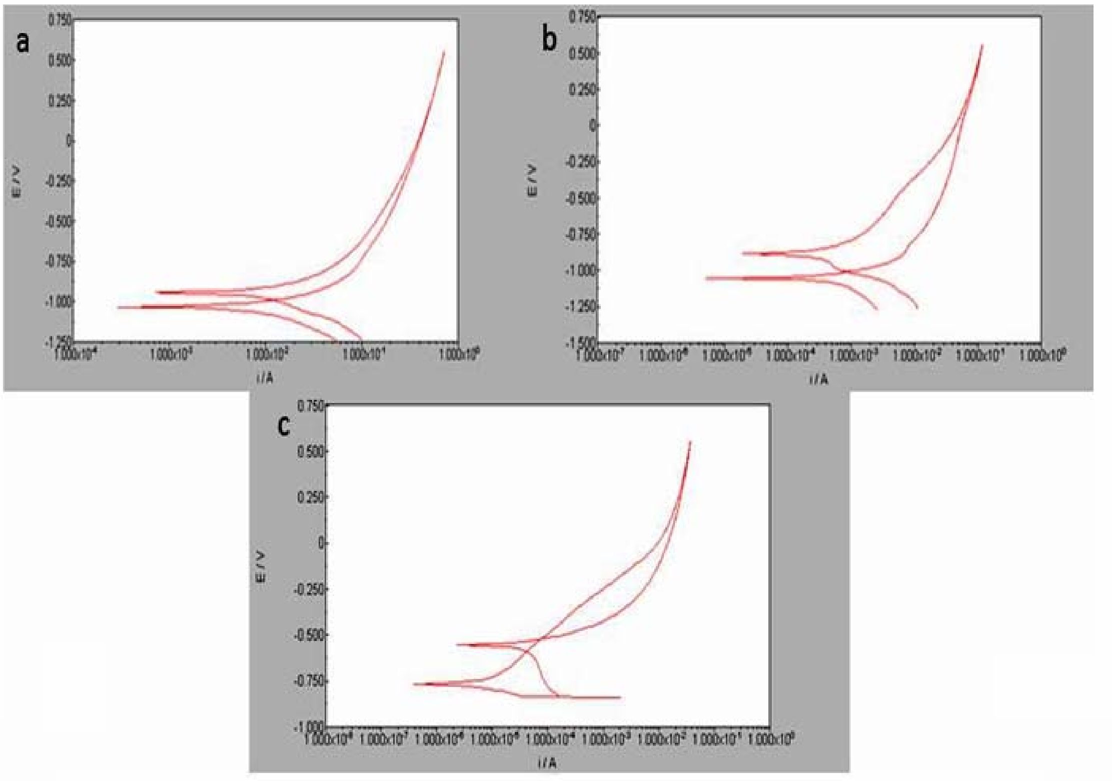


Fig. 4: Cyclic Potentiodynamic Polarization curve of a) substrate b) Zn and c) Zn-Al-ST coatings samples in 3.65% NaCl solution.

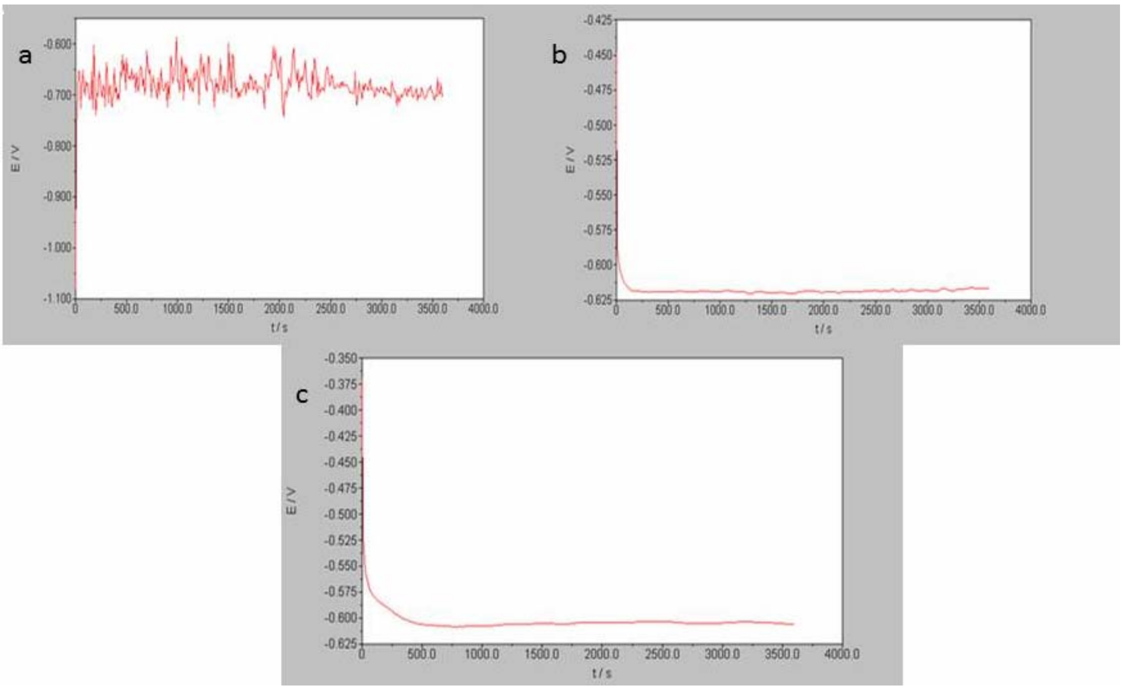


Fig. 5: Open Circuit Polarization curve of a) substrate b) Zn and c) Zn-Al-ST coatings samples in 3.65% NaCl solution

The potential from the OCP scan showed mild steel have -1.100 V, Zn was -0.450 V and for Zn-Al-ST was -0.375 V. The coatings however have a significant influence on the corrosion resistance potential as a result of additive inclusion. This obviously indicates that deposits are advantageous for substrate improvement. Moreso, when comparing the potential difference justified result was obtained with Zn having 0.550 and Zn-Al-ST with 0.630 V over the mild steel.

In other word, Al-ST in Zn interface on mild steel shifts potential positively with open circuit time and the trends became linear due to the passive film formation thereby increasing the corrosion resistance of the steel substrate. The results obtained from cyclic potentiodynamic polarization test agree with the open circuit polarization. At this point, the metals can be said to be protected with a more pronounce thin film than Zn deposits. It is worthy to note that corrosion resistance of Zn with Al-ST interface is much higher than that of Zn without Al-ST interface.

The corrosion potential difference of Zn and Zn-Al-ST was about 0.085 V as indicated in Fig. 5b-c which has positive effects on the polarization resistance of the substrate. The impact of Al-ST addition with the Zn on the substrate indicated higher corrosion potential than ordinary zinc deposit. This may be attributed to oxidation of Al particulate and absorption of the thin films caused by the leveling agent originated from the addition of the Solanum tuberosum juice extract and the complex chemical composition noticed on the surface of the modified substrate. Hence, the additive induced might cause structural modification that will tend to disallow the penetration of oxygen into the surface of the modified Zn bath resulting into passive corrosion resistance.

Experimental

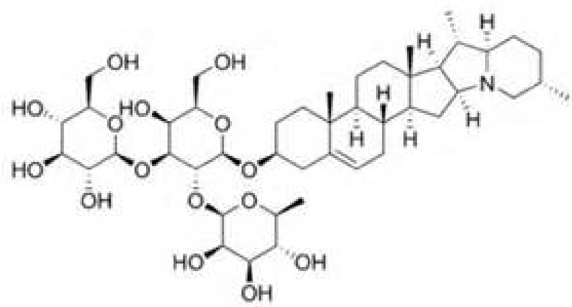
Electrodeposition Process

The chemicals used were of AR grade. Distilled water was used for the preparation of solutions. The electroplating of Zn-Al-ST was achieved through a designed cell consisting of two anode and cathode electrodes in between. Locally flat mild steel of (40 mm x 20 mm x 1 mm) with chemical composition as show in Table-1 was used as substrate and zinc sheets (30 mm x 20 mm x 1 mm) were used as anodes. Deposition was achieved by adding the prepared 10% ST juice addition agents into 1000ML bottom flask in addition with 99.5 % pure aluminum at 10g/l, ZnCl (120g/l), KCl (80g/l) and H_3BO_4 (20g/l). 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, 400 µm, 800 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^o or 180^o at intervals 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.

The prepared electrolytically metal substrate was immersed in a solution containing dissolved bath constituent admix salts. The cathode was connected to the negative terminal of the rectifier of the electroplating bath while the anode was also connected to the positive terminal of the rectifier. The voltage was kept at 1.0 V, 0.2 A for 20 minutes with the depth of immersion and distance from cathode to anode kept constant. Immediately after the plating, rinsing was done in distilled water and air dried. The chemical composition of the mild steel is showed in Table-2. The natural Potato tuber (solanum tuberosum*)* used was obtained from materials shop in Pretoria, South Africa with molecular structure shown in Fig. 1.

Table-2: Chemical composition of the mild steel.

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



Molecular structure of Solanum tuberosum.

Extracted Fermentation Process

The extracted juices from ST tuber were used as the electrodeposition additive, in different concentrations. The solanum tuberosum tuber weighed 2Kg were collected. The tubers were cut into smaller pieces and blended using a blending machine. The blended tubers were then soaked in 500 ml containers containing water. These were filtered and the solution was left to evaporate at room temperature for four days to have a highly concentrated juice extracts. The solanum tuberosum tuber extract was stored in save, clean airtight bottles and refrigerated.

Characterization of the Electrodeposited Samples

SEM/EDS Characterisation

The structural surface of the electrodeposits were observed using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) (model: Joel 6100) to examine the surface topography and morphology of the plated test specimens. X-ray diffreaction (XRD) analysis was also conducted.

Electrochemical Test

For corrosion resistance study, cyclic potentiodynamic polarization and open circult polarization tests were carried out on the deposited samples as well as the as-received. 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). –1.51 V to +1.5V scanned potential at a scan rate of 0.0012V was used for the potentiodynamic study.

Conclusions

Zn coating in the presence of Al- solanum tuberosum (ST) was successfully deposited. The additive used in this study was eco-friendly and eatable agricultural product. The coating was cohesive, brighter and possessed good corrosion resistance. XRD results of the deposits shows that the Zn-Al-ST constituent has some preferred orientation phase Zn, Zn_2Al_3.Sn and ZnAlO. The EDS analysis also affirmed the existence Zn, Al and other phyto-chemical agent from ST responsible for the adhesion of the deposited on the steel. The incorporation of the particles and the juice extract help in the enhancement of corrosion resistance by providing corrosion barriers within the process and by filling the crevices and gaps within coatings.

Acknowledgements

This material is based upon work supported financially by the National Research Foundation. The authors also acknowledge the support from Tshwane University of Technology and Technology Innovation Agency (TSC) Pretoria, South Africa which helped to accomplish this work.

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