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Electrodeposition of Nanocrystalline Zinc on Steel Substrate from Acid Sulphate Bath and its Corrosion Study

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ABSTRACT

Nanocrystalline zinc was electrodeposited on steel substrates from acid sulphate bath. The condensation product formed between Glycyl-glycine (GGL) and Veratraldehyde (VTL) was used as brightener. The effect of bath constituents, pH, temperature and current density were optimized through Hull cell studies. Potentiodynamic polarization, cathodic current efficiency, throwing power studies were carried out. Salt spray test and electrochemical measurements showed that nanocrystalline zinc coatings have better corrosion resistance. The inclusion of addition agent in the deposit was confirmed by FT-IR studies. The surface morphology of the zinc deposit was investigated through SEM studies. The crystal structure was studied by X-ray diffraction and TEM analysis.

Key words: Acid sulphate bath, Corrosion behavior, Hull cell studies, Nanozinc coating, TEM analysis.

INTRODUCTION

Nanostructured materials (1–100 nm) are known for their outstanding mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction [1]. Significant progress has been made in various aspects of synthesis of nano-scale materials. The focus is now shifting from synthesis to manufacture of useful structures and coatings having

greater wear corrosion resistance. Electrodeposition is a versatile technique for producing nanocrystalline materials [2]. It is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size dependent [3]. The grain size of the electrodeposits depends on the deposition parameters such as pH [4], deposition technique [5], current density [3] and substrate [6], as well as on the type and the amount of additives included in the electrolyte [7].

The use of additives in electrodeposition solutions is extremely important due to their influence on the growth and structure of the resulting deposits. The presence of additives has been shown to influence physical and mechanical properties of electrodeposits such as grain size, brightness, internal stress, pitting and even chemical composition [8].

Electrodeposition technique can yield porous-free finished products that do not require subsequent consolidation processing. Further this process requires low initial capital and provides high production rates with few shape and size limitations [9].

During the past decade, extensive work on the characterization of nanocrystalline materials has been conducted. However, there are only a few experimental tensile studies of nanocrystalline materials with a grain size equal or less than 25 nm [10-11]. One reason for the scarcity of results is the difficulty in processing pure and defect free materials [12].

In this investigation nanocrystalline zinc coating was obtained from simple acid sulphate bath. A non-toxic and water soluble condensation product was synthesized and used as brightener for electrodeposition [13]. An attempt has been made to study the bath characteristics and the effect of bath constituents and bath variables on the corrosion behavior of nanocrystalline zinc deposit.

EXPERIMENTAL SECTION

2.1. Preparation of nanocrystalline zinc coatings

All the solutions were prepared from AR grade chemicals (s.d.fine chemicals, Mumbai, India) and double-distilled water. The standard Hull cell of 267-ml capacity was used to optimize the bath constituents and bath variables [14]. The Hull cell experiments with the bath solution given in Table 1 were carried out without agitation. The pH of bath solution was measured using a digital pH meter (Equipetronix, model: 7020) and adjusted with 10% sulphuric acid or sodium bicarbonate solution. Zinc plate of 99.99% purity was used as anode and activated each time by immersing in 10% HCl followed by water wash. Mild steel (AISI-1079, composition C 0.5%, Mn 0.5%, P and S 0.05% and rest Fe) plates of standard Hull cell size were mechanically polished using emery paper (320-800 grit size) to obtain a smooth surface and degreased by dipping in boiling trichloroethylene. The scales and dust on the steel plates were removed by dipping in 10% HCl solution and then subjected to electrocleaning process. These steel plates were washed with distilled water and used for the experiments as such. After electrodeposition the plates were subjected to bright dip in 1% nitric acid for 2-3 s followed by water wash and drying. The nature and appearance of zinc deposit was carefully observed and recorded through Hull cell codes (Figure 1).

The additive was synthesized by the condensation of equimolar amounts of GGL (1 g) with chemical formula, $C_4H_8N_2O_3$ and VTL (1.2589 g) with chemical formula, $C_9H_{10}O_3$, under reflux conditions for 3 h at 343 K in ethanol medium (20-ml) [15]. The completion of the reaction was monitored by TLC. The resulting product was diluted to 100-ml with distilled water and a known amount of this solution was added to the electroplating bath solution. The bath solution was stirred for 30 min before conducting the experiments.

For the measurement of adherence and ductility pre-cleaned mild steel plates of $4 \times 6 \text{ cm}^2$ area were electrodeposited in a 2.5 l rectangular cell. Experiments were done in triplicate. Standard experimental procedures were adopted for the measurement adherence and ductility of the zinc deposit [16]. In above studies the average thickness of the deposit was 20 μm .

The average thickness of the deposit was calculated using the formula

$$T = \frac{W}{a \times d}$$

where T is the average thickness of the deposit in μm , 'W' is the weight of the metal plated, 'a' is the plated area in square centimeters and 'd' is the density of metal in g/cm^3 .

2.2. Current efficiency and throwing power measurements

The cathodic current efficiencies (CCE) as the percentage of the total current usually employed for the cathode deposition of the metal. This is calculated from the relationship

$$\%CCE = \frac{\text{Weight of the metal actually deposited}}{\text{Weight of the metal calculated from the quantity of electricity is passed}} \times 100$$

Electrodeposition was carried out for 10 min in each case.

Throwing power (TP) was measured using Haring-Blum cell. A porous zinc anode was placed between two plane parallel steel cathodes filling the rectangular cell cross section. The cathodes distance ratio was 5:1 from the central anode. The percentage throwing power was calculated from Field's formula [17].

where

$$M = \frac{\text{The weight of the deposit on nearer cathode}}{\text{The weight of the deposit on farther cathode}}$$

$$\%TP = \frac{L - M}{L + M - 2} \times 100$$

and

$$L = \frac{\text{Distance of farther cathode from anode}}{\text{Distance of nearer cathode from anode}}$$

2.3. Electrochemical studies

The effect of additives on corrosion resistance of the zinc deposits was studied in 3.5% NaCl solution by galvanostatic polarisation method. A three electrode cell assembly was used. The electrodeposited steel specimen with an exposed area of $1 \times 1 \text{ cm}^2$ was used working electrode (WE). A platinum foil was used as the counter electrode (CE) and saturated calomel as reference electrode (RE). The working electrode was immersed in 3.5% NaCl solution for 20 min before applying the current to establish a stable rest potential. The WE was polarized from the rest potential (OCP) against SCE. The current was increased in steps from zero and the potential between the WE and SCE was measured at a steady state. The corrosion potential (E_{corr}) and corrosion current (i_{corr}) were obtained using Tafel extrapolation method.

The cathode potential was recorded galvanostatically with respect to saturated calomel electrode at different current densities (i) and the polarisation curve was obtained by plotting V vs i .

2.4. Scanning electron microscope (SEM) studies

The grain-size of the electrodeposit was observed using scanning electron microscope (model JEOL-JSM-35 LF at 25kV). SEM images of the electrodeposits before and after electrochemical and chemical studies were taken to assess the inhibition property of the deposit.

2.5. Salt spray test

Salt spray test was carried out in accordance with ASTM B 117 specifications. The electrodeposited steel samples of $5 \times 5 \text{ cm}^2$ area under different experimental conditions were taken for this study [18]. The specimens were carefully observed for every 24 h and the time taken for the formation of white rust was recorded.

2.6. X-ray diffraction studies

Powder X-ray diffraction patterns were recorded for the zinc deposits obtained from the bath solution with and without additive using Philips TW 3710 X-ray recorder. The nickel-filtered $\text{Cu-K}\alpha$ radiations were used for determining the lattice parameter, crystallographic texture and average grain size of the deposit. The grain-sizes of the coating were measured through the Scherrer's equation.

2.7. TEM studies

TEM was performed using JEOL/JEM-200LR microscope equipped with field emission gun. An accelerating voltage of 200 kV was used. Samples were dispersed in acetone and a drop of the solution was placed on the amorphous copper grid. The liquid was evaporated and the samples were introduced into the microscope.

RESULTS AND DISCUSSION

3.1. Hull cell studies

3.1a. Effect of additive

The Hull cell experiments with basic bath solution (Table 1) gave coarse dull deposit in the current density range $1\text{-}5 \text{ Adm}^{-2}$ at 1A cell current. To improve the nature of the deposit condensation product prepared from GGL and VTL was added to the bath solution. The additive

contains electroactive groups such as $-C=N-$ and $-NH_2$ in addition to aromatic ring. In most of the cases these groups form complexes with zinc metal ions and controls the rate of metal deposition [19]. The deposition potential for zinc ions in presence of additive shifted to more cathodic direction and leads to a regular and uniform crystallization of the deposit. According to the Hull cell results, the appropriate concentration of additive in plating bath to get mirror bright deposit was 20 ml/l. The effect of additive on deposit nature is shown in (Figure 1b).

3.1b. Effect of zinc sulphate

Zinc sulphate is the main salt of zinc ions in electroplating operation. There is a close relation between the concentration of zinc sulphate and appearance of plating layer in Hull cell experiment. In order to get highly corrosion resistant bright zinc deposit it is essential to strike a balance between amount of zinc sulphate in the bath solution. To find out the effect of zinc sulphate concentration on the deposit nature, zinc sulphate concentration was varied from 60-300 g/l. According to the Hull cell experiment, the appropriate quantity of zinc sulphate in plating solution was 240 g/l. At this concentration the deposit was bright in the current density range $0.5-5 \text{ Adm}^{-2}$. At lower concentration ($< 240 \text{ g/l}$), bright deposit was observed in the current density range between $2-6 \text{ Adm}^{-2}$. At lower current density region uncoated and at high current density region burnt deposits were obtained. The effect of zinc sulphate on deposit nature is shown in Figure 1c.

3.1c. Effect of sodium sulphate

To increase the conductivity of the bath solution certain conducting salts having chlorides and sulphates ions were added. To find out the effect of sodium sulphate concentration on the deposit nature, concentration of sodium sulphate was varied from 10-60 g/l. At a concentration of 40 g/l, the Hull cell panels were bright in the current density range of $0.5-5 \text{ Adm}^{-2}$. The effect of sodium sulphate on deposit nature is shown in Figure 1d.

3.1d. Effect of Boric acid

The presence of boric acid in the bath solution generally results in an increase of current efficiency of metal deposition and hence nucleation density of the deposit. These effects have been attributed to the adsorptive interaction of boric acid at the electrode surface. Also, boric acid acts as buffer to maintain the pH of the electrolytic bath [20].

To see the optimum concentration of boric acid, the concentration was varied from 10-60 g/l keeping the concentrations of zinc sulphate and sodium sulphate at 240 g/l and 40 g/l, respectively. Lower concentration of boric acid ($< 20 \text{ g/l}$) gave bright deposit in the current density range $0.5-3 \text{ Adm}^{-2}$. At a concentration of 40 g/l, mirror bright deposit in the current density range $0.5-5 \text{ Adm}^{-2}$ was obtained. The concentration of boric acid was fixed at 40 g/l as optimum in the bath solution (Figure 1e).

3.1e. Effect of Cetyl trimethyl ammonium bromide (CTAB)

Fine-grained and brilliant coatings obtained only if appropriate surfactants are introduced into the bath solution [21]. The surfactants exhibit complexing property towards metal ions and thereby control the deposition mechanism. They have a tendency towards adsorption on the surface of the cathode due to which the crystallization process becomes appropriate. Surfactants

may also affect the kinetics of individual stages of the zinc deposition process and hence improves the physical and chemical properties of the deposits.

The concentration of CTAB was varied from 1-5 g/l (Fig. 1f). At low concentration (< 2 g/l), the bright deposit was observed in the current density range between 1-4 Adm^{-2} . In the low current density region dull and at high current density region burnt deposits were obtained. At a concentration of 2 g/l satisfactory bright deposits was obtained in the current density range of 0.5-5 Adm^{-2} at 1 A cell current.

3.1f. Effect of pH and temperature

The pH of plating bath has great effect on bright current density region on Hull cell cathode. At high pH the deposit may becomes spongy or porous, where as at low pH of the bath may lead to cathode hydrogen evolution and a consequent decrease in current efficiency, throwing power. This in turn may lead to an accumulation of hydroxyl ions in the vicinity of the cathode and consequent precipitation of the basic salt, which may get included in the deposit, there by altering the deposit properties [16]. The Hull cell experiments showed that at a pH of 3 the cathodes were bright in the current range 0.5-5 Adm^{-2} at 1 A cell current. At low pH (< 3) the low current density region was uncoated and at high pH (> 3) the high current density region covers burnt deposit (Figure 1g).

Hull cell experiments showed that the optimum temperature range to get bright deposit was 293-303 K. At higher temperature (> 303 K) the supply of ions to the cathode is hastened so that bad quality of deposit is obtained. And also rate of growth of nuclei is increased, leading to coarse grained deposit. Hull cell patterns showing the effect of temperature are depicted in the Figure 1h.

3.1g. Effect of current density

There is a close relation between appearance of plating layer and cathode current density. The Hull cell experiments were carried out at different cell currents (1-4A) for 10 min using optimum bath solution. The Hull cell patterns are shown in Fig. 1i. At a cell current of 1A, the deposit was bright in the current density range of 0.5-5 Adm^{-2} . At a 2A, the deposit was bright in the current density range of 1.5-5 Adm^{-2} . At higher cell currents (> 3A) the Hull cell cathodes covered with burnt and trees like deposit at high current density region. This was attributed to the high hydrogen discharge which leads to an increased hydroxyl ion concentration and subsequent precipitation of metal hydroxides or basic salts of the metals. The inclusion of these metal hydroxides gave spongy-black layer on the cathode surface. Because of the rapid discharge of ions to form metal atoms, there was likelihood of the nuclei growing outward toward the bulk of the solution with high metal content. Under these conditions nodule formation or treeing of the deposits occurred [16]. Based on the above observation bright current density was found to be 0.5-5 Adm^{-2} . Optimum bath composition and operating conditions were given in Table 2.

3.2. Current efficiency and throwing power studies

Current efficiency and throwing power were measured at different current densities by using optimized bath solution. At 1.0 Adm^{-2} , the current efficiency was found to be 94%. At a current density of 2 Adm^{-2} , the current efficiency was found to be 96%. With increase in the current

density above 3 Adm^{-2} , the current efficiency was found to be decreased and at 5 Adm^{-2} it was 89%.

However, increasing the current density from $1\text{-}5 \text{ Adm}^{-2}$, decreases the throwing power of the bath solution from 26% to 24%, as a result of increased polarization. The variation of throwing power and current efficiency with current density at pH 3 is given in Table 3.

3.3. Polarization studies

The polarization curves showed that the presence of condensation product in the bath solution shifts the cathodic potential to more negative values (Figure 2). Generally, condensation product containing electroactive functional groups like -C=N- , $\text{-NH}_2\text{-}$ etc, adsorb at the electrode surface and reduce the surface stress at the gas-electrolyte interface.

3.4. Corrosion resistance studies

Figure 3 and 4 present the effect of additive on corrosion behavior zinc deposits in 3.5% NaCl solution. The values are given in Table 4. From the figures it can be seen that the i_{corr} values for zinc deposits obtained were considerably low. Hence the deposit obtained in the presence of condensation product showed maximum corrosion resistance.

3.5. Salt-spray test studies

The neutral salt spray test was conducted for the zinc deposits. The fog of droplets accumulated on the surface of the articles facilitates the corrosion resulting in zinc salts called white rust. The number of hours for the formation of white rust has been indication of the corrosion resistance. The higher corrosion resistance delays the production of white rust. In the present case zinc deposit obtained from the basic bath produced white rust after 24 h and the bright deposit produced white rust after 96 h. Chromate passivated article did not show white rust even after 96 h of testing. This confirmed the enhancement of corrosion resistance of zinc in presence of condensation product.

3.6. Surface morphology studies

The nature of crystal growth in the presence and absence of condensation product is explained with the help of SEM photomicrographs (Figure 5). Figure 5A is the SEM photomicrograph of the deposit obtained from the basic bath shows coarse-grained deposit having irregular crystal size. SEM photomicrograph of deposit obtained from the optimum bath shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit (Figure 5B).

The zinc deposits obtained from the bath with and without condensation product were treated in 3.5% NaCl solution for 15 days. The large number of corrosion products are noticed in the SEM image of zinc coated sample obtained from basic bath (Figure 6A). Very little corrosion is observed on the zinc deposits coated in presence of condensation product (Figure 6B). Figure 7A and 7B represents the SEM images of pure zinc and bright zinc respectively, after cathodic polarization in 3.5% NaCl solution. SEM images of zinc deposits of 7.5 and 15 μm after potentiodynamic polarization in 3.5% NaCl solution is shown in the Figure 8 (Figure 8A,B) and Figure 9 (Figure 9A,B) respectively. The SEM studies indicated that the deposits obtained in

presence of additive showed higher corrosion resistance and the similar results obtained by weight-loss and electrochemical measurements.

3.7. Adhesion and porosity studies

Standard bend test was used to measure both adherence and ductility of zinc deposits. Mild steel panels of 1mm thick ($1 \times 10 \text{ cm}^2$ area) were electroplated with zinc to a different thicknesses (5-20 μm). The samples were subjected to bending through 180° . No crack or peel off in the deposit was noticed even after 180° bending. This indicated good adherence and ductility of zinc deposit on steel.

3.8. X-ray diffraction studies

Figure 10 and 11 show X-ray diffraction patterns of the zinc electrodeposits obtained from the basic and optimum bath respectively. All the deposits were crystalline in nature and have hexagonal structure. The observed ' 2θ ' value is in good agreement with the standard values for zinc deposition (Joint committee on Powder Diffraction System/ASTM File No. 1* 40831Zn). Crystal size of the deposit was determined from the full wave at half maximum (FWHM) of the X-ray peaks present on the diffractogram and corresponding results are presented in Table 5. The X-ray patterns of the deposit in the presence of condensation product showed a broadening of the diffraction peaks. This broadening can be attributed to the decrease in grain size. The average grain size of the zinc deposit obtained from bath solution in presence and absence of condensation product is 19 nm and 38 nm respectively.

3.9. TEM studies

Figure 12 shows TEM bright-field and selected area diffraction pattern (SADP). Photomicrographs revealed that the grain size of zinc deposit obtained in presence of condensation product found to be around 15 nm. This shows the refinement of grain-size in presence of brightener.

Table -1: Basic bath composition and operating conditions

Bath composition	Quantity (g/l)	Operating conditions
ZnSO ₄ .7H ₂ O	200	Anode: Zinc metal (99.99%) Cathode: Mild steel Temperature: 293-303 K Cell current: 1 A
Na ₂ SO ₄	30	
H ₃ BO ₃	30	
CTAB	1	

Table -2: Optimum bath composition and operating conditions

Bath composition	Quantity (g/l)	Operating conditions
ZnSO ₄ .7H ₂ O (g/l)	240	Anode: Zinc metal (99.99%) Cathode: Mild steel Temperature: 293-303 K Bright current density range: 0.5-5 Adm^{-2} Agitation: Air
Na ₂ SO ₄ (g/l)	40	
H ₃ BO ₃ (g/l)	40	
CTAB (g/l)	2	
Condensation product (GGL-VTL) (ml/l)	20	

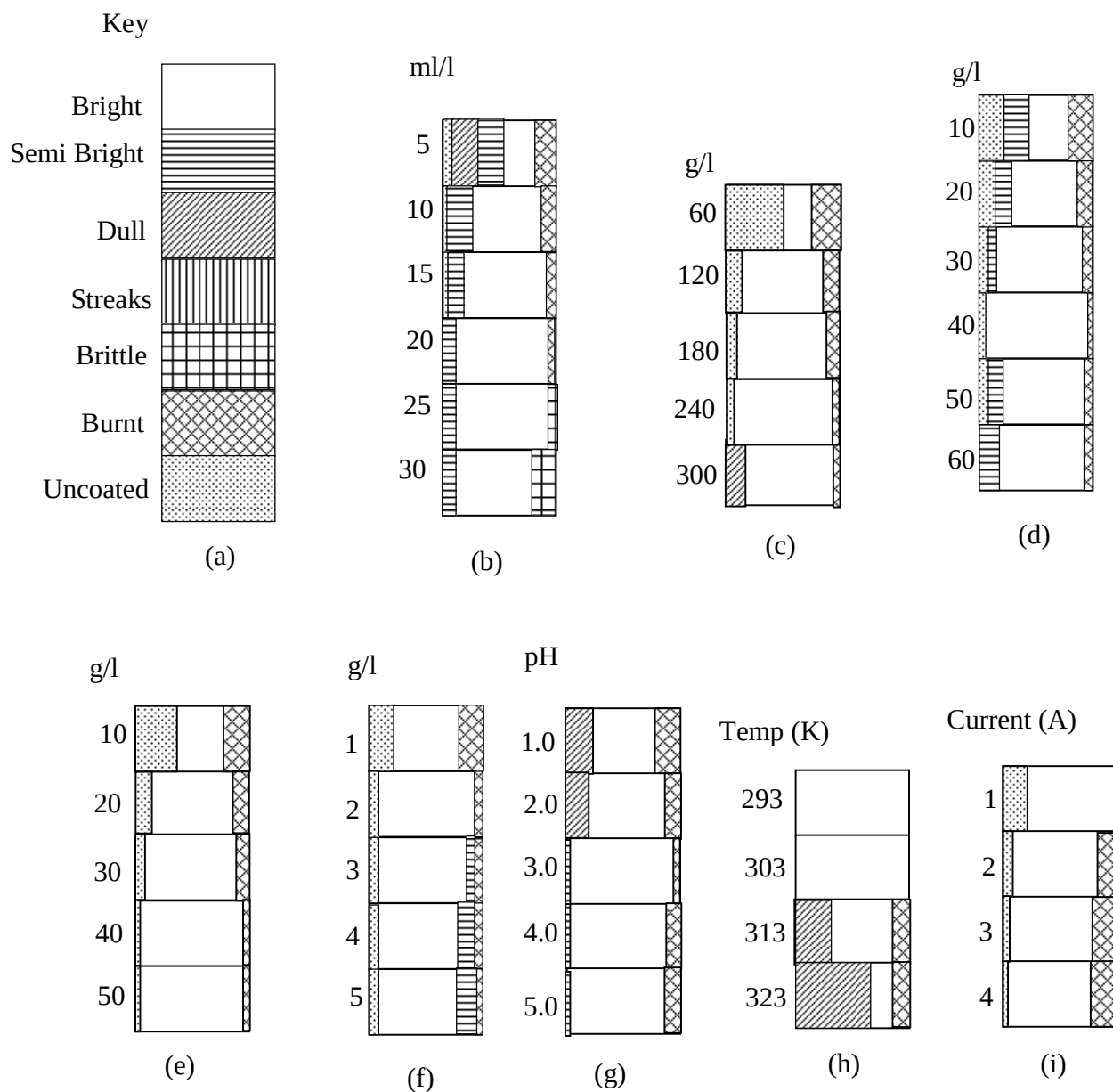


Fig. 1. Hull cell figures: (a) Key, (b) Effect of additive, (c) Effect of ZnSO_4 , (d) Effect of Na_2SO_4 , (e) Effect of H_3BO_3 , (f) Effect of CTAB, (g) Effect of pH, (h) Effect of temperature, and (i) Effect of cell current.

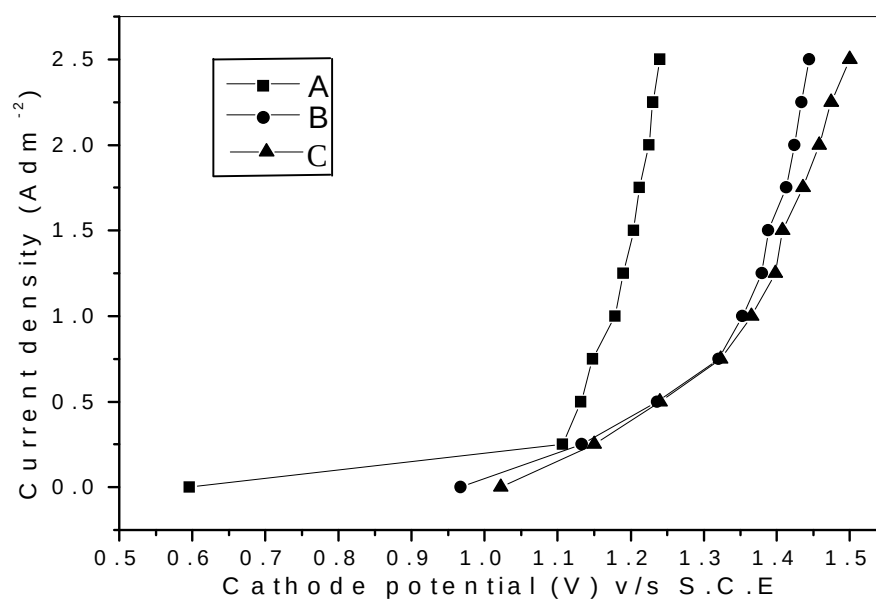


Fig. 2. Effects of addition agents on cathodic potential. {(A) ZnSO_4 , (240 g/l) + Na_2SO_4 (40 g/l) + H_3BO_3 (40 g/l) + CTAB (2 g/l) [BB]; (B), BB + GGL-VTL (20 ml/l)}.

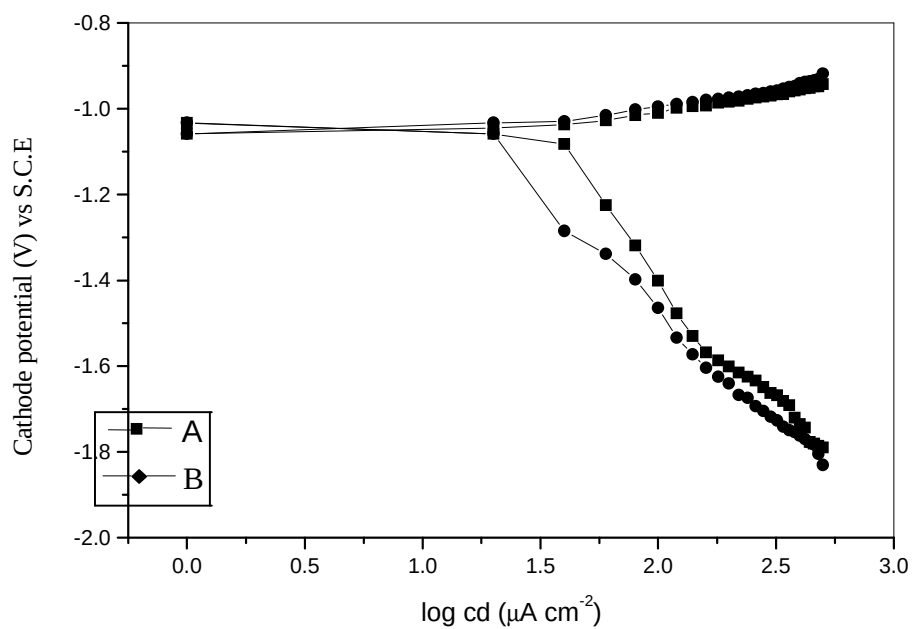


Fig. 3. Typical potentiodynamic polarization curve for coating thickness $7.5 \mu\text{m}$ in 3.5% NaCl solution. (A), Basic bath; (B), Optimized bath.

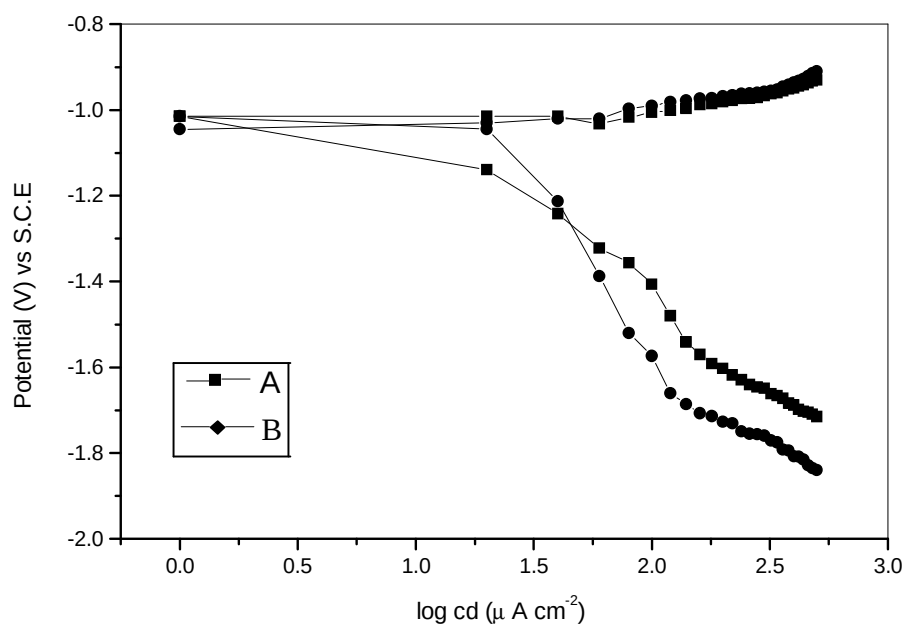


Fig. 4. Typical potentiodynamic polarization curve for coating thickness 15 μm in 3.5% NaCl solution. (A), Basic bath; (B), Optimized bath.

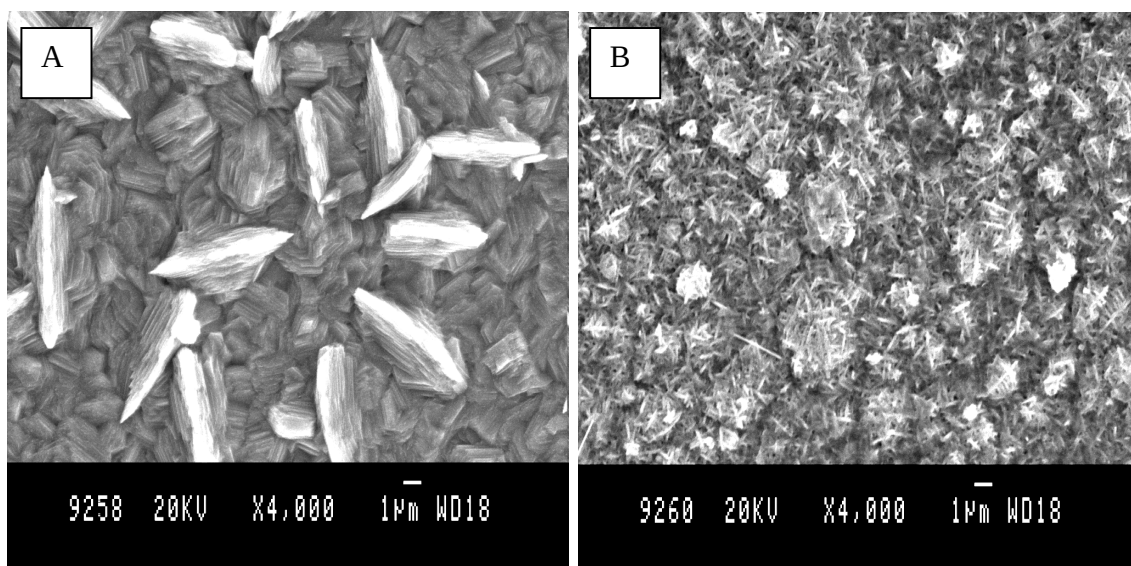


Fig. 5. SEM photomicrographs of the deposits obtained at 3 Adm^{-2} in the presence and absence of addition agents at 298 K: (A) Basic bath (BB), (B) BB + CTAB (C) Optimized bath, (D) Passivated deposit.

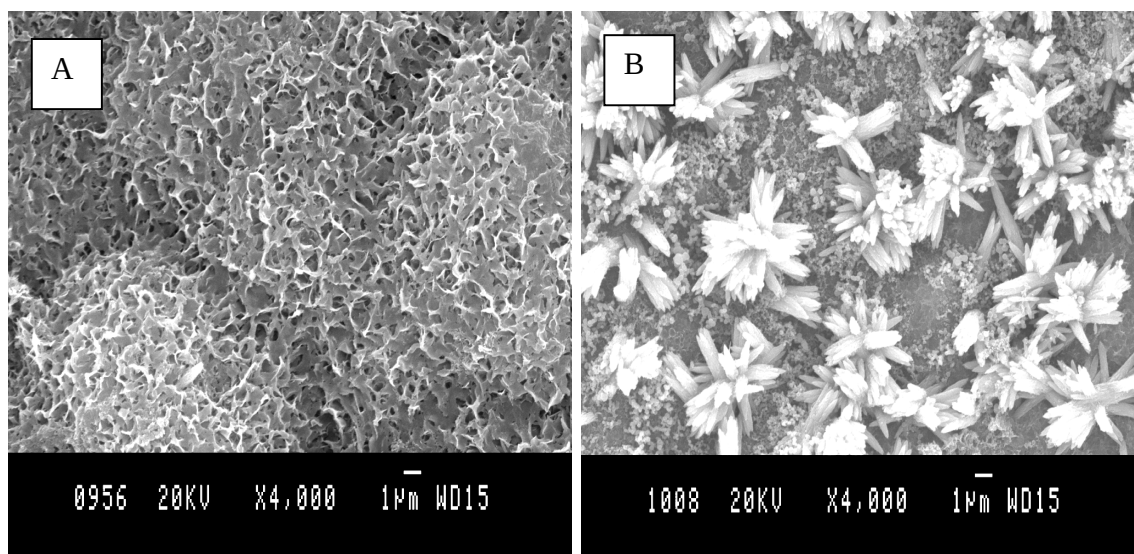


Fig. 6. SEM images for two samples after 15 days immersion 3.5% NaCl solution (A) without additive, (B) with additive

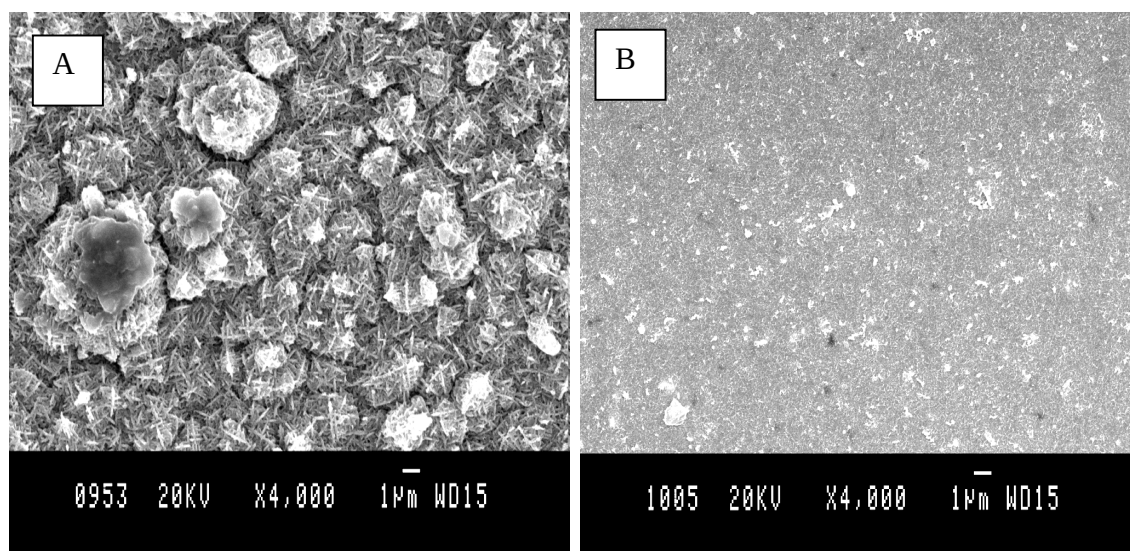


Fig. 7. SEM images for two samples after cathodic polarisation, (A) without additive, (B) with additive

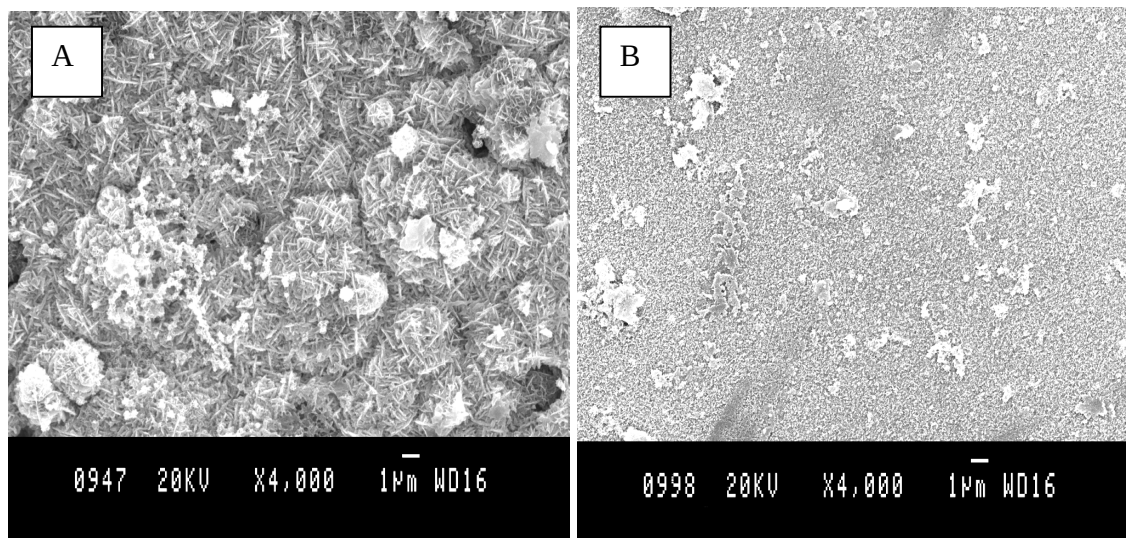


Fig. 8. SEM images for two samples of coating thickness 7.5 µm after potentiodynamic polarisation (A) without additive, (B) with additive

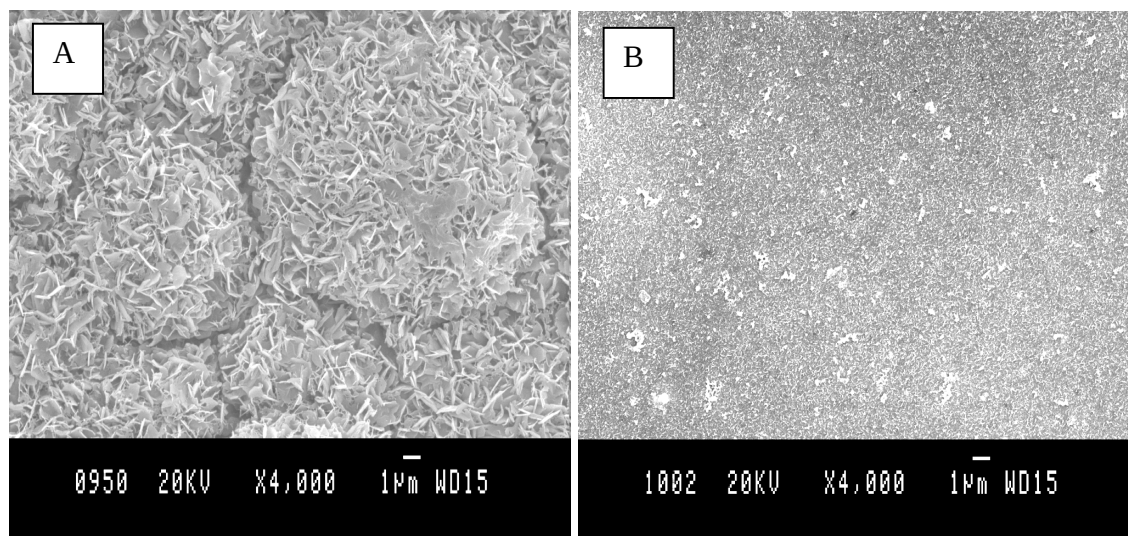


Fig. 9. SEM images for two samples of coating thickness 15 µm after potentiodynamic polarisation (A) without additive, (B) with additive

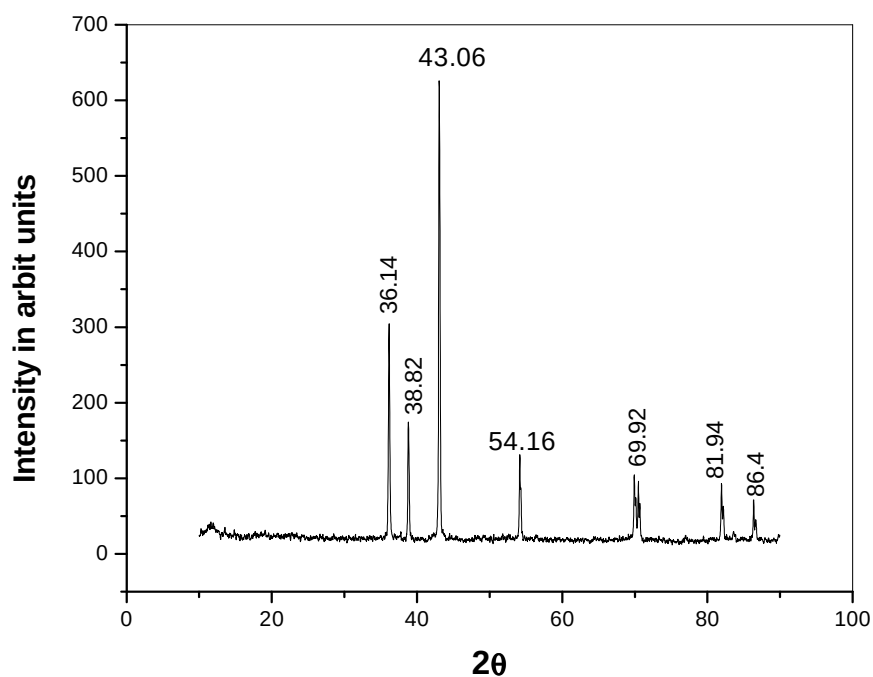


Fig. 10. X-Ray diffraction pattern of the zinc deposited from the electrolyte without additive.

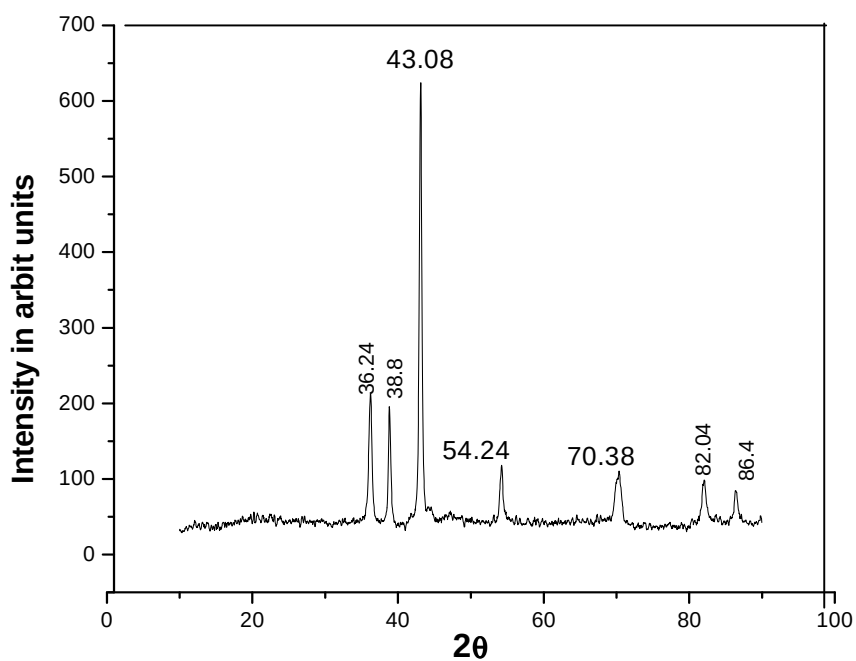


Fig. 11. X-Ray diffraction pattern of the zinc deposited from the electrolyte with additive.

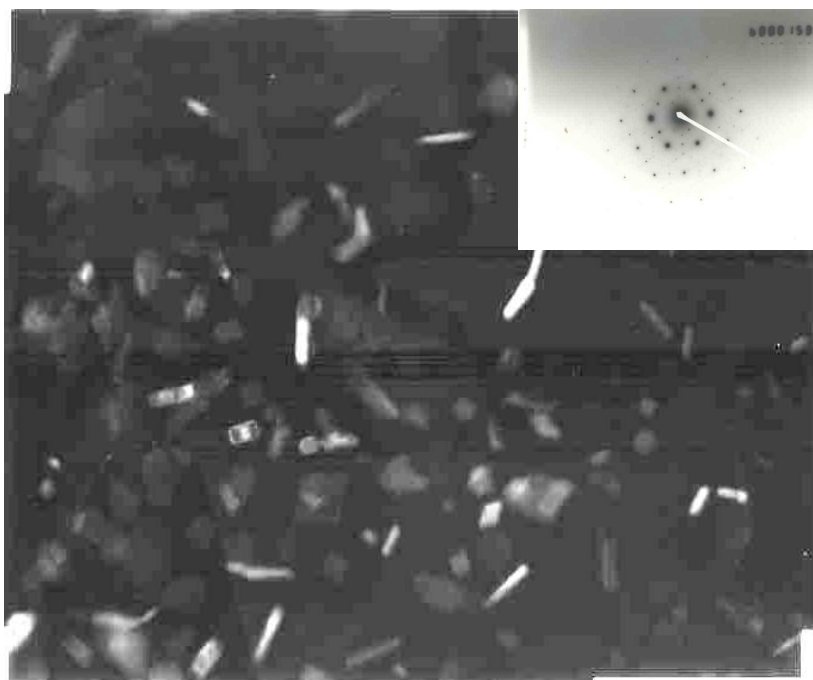


Fig. 12. TEM photomicrograph of the zinc deposited from the electrolyte with additive

Table- 3: Current efficiency and throwing power for optimum bath solution at different current densities

Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1.0	94	25
2.0	96	26
3.0	95	26
4.0	92	25
5.0	89	24

Table- 4:Galvanostatic polarization in 3.5% NaCl solution

Bath system E_{corr} i_{corr}	Deposit thickness (μm)	E_{corr} (-mV vs SCE)	i_{corr} ($\mu\text{A cm}^{-2}$)
Basic bath	7.5	1550	35.48
Optimum bath		1300	19.95
Basic bath	15	1100	28.18
Optimum bath		1200	15.84

Table- 5:Parameters derived from XRD data

Bath system	Average crystal size (nm)	2 θ		hkl
		Observed	Standard	
Basic bath	37.5	36.153	36.295	(0 0 2)
	44.8	43.09	43.23	(1 0 1)
	76.97	86.395	86.553	(2 0 1)
Optimum bath	17.41	36.200	36.295	(0 0 2)
	19.41	43.120	43.23	(1 0 1)
	19.46	86.400	86.553	(2 0 1)

CONCLUSION

A nanocrystalline zinc was electrodeposited on mild steel from simple acid sulphate bath. The addition agent is a simple condensation product formed between GGL and VTL, which is water soluble and non-toxic. The developed bath had about 26% throwing power, 96% cathode current efficiency and 0.5-5 Adm^{-2} current density range. The deposit obtain from optimum bath are highly corrosion resistance as it was evident by SEM and electrochemical studies.

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