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NANOCRYSTALLINE ZINC COATING ON STEEL SUBSTRATE USING CONDENSATION PRODUCT OF GLYCYL-GLYCINE (GGL) AND VANILLIN (VNL) AND ITS CORROSION STUDY

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ABSTRACT

Nanostructured surface layer of zinc was electrodeposited on mild steel by simple electrochemical route. Bath composition, pH, current density and temperature were optimized through Hull cell experiments. Salt spray tests, cyclic voltammetric and linear polarization measurements were made in order to assess the corrosion behavior of the zinc deposit. The bath in presence of GGL and VNL produced highly corrosion resistant bright zinc deposit. The surface morphology and thickness of the zinc deposits were studied by scanning electron microscopic (SEM) studies. The preferred orientation and average particle size of the zinc electrodeposits were obtained by X-ray diffraction (XRD) analysis.

Key words: Electroplanting, Electrochemical measurements, Nanocoating, Steel substrate.

INTRODUCTION

Developments in the field of uniform nanometer sized particles have been studied extensively in recent times because of their technological and fundamental scientific importance[1]. These nanomaterials exhibit very interesting electrical, optical, magnetic, chemical and related surface properties, which is entirely different from the respective bulk materials[2,3]. Nanocrystalline materials may be produced in a number of ways, including gas condensation, spray conversion, ball milling and electrochemical deposition[4]. However,

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electrodeposition technique can be applied to produce nanostructured materials for corrosion studies. This technique can yield porosity free finished products that do not require subsequent consolidation processing. Further, this process requires low initial capital investment and provides high production rates with few shape and size limitations[5-7].

The properties of the deposits depend on a number of factors such as composition and metallurgical structure (grain size, growth orientation), which are in turn affected by the deposition conditions. These parameters include current density, electrolyte composition, pH and temperature as well as on the type and the amount of additives included in the electrolyte[6,8-11]. Local control of these factors is essential for the successful electrodeposition of high aspect ratio geometries with well defined properties.

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[12-16].

In the present work, effect of condensation product on zinc deposition was investigated because of its high solubility in aqueous solutions and excellent biodegradability. An attempt has been made to study systematically the bath characteristics and the effect of organic additive on corrosion behavior.

EXPERIMENTAL

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. The Hull cell experiments with the bath solution (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% H_2SO_4 or $NaHCO_3$ 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 different grades of emery paper 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% HNO_3 for 2-3 s followed by water wash and drying. The nature and appearance of zinc deposit was carefully observed and recorded the current density range.

Table 1: Bath composition and operating conditions

Bath composition & variable	Quantity range (g/L)	Optimum quantity (g/L)
$ZnSO_4.7H_2O$	50-300	240
$Na_2SO_4.6\ H_2O$	10-60	40
H_3BO_3	10-50	30
CTAB	1-4	2
Condensation product (GGL-VNL)	5-50 mL	30 mL
pH	2-5	3
Temperature	293-303 K	293-303 K
Cell current	1-3A	2A

The additive was synthesized by the condensation of equimolar amounts of GGL (1.0 g) with chemical formula, $C_4H_8N_2O_3$ and VNL (1.15 g) with chemical formula, $C_8H_8O_3$, under reflux conditions for 3 h at 343 K in ethanol medium (20 mL)[17]. 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 × 6 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 of adherence and ductility of the deposit. In the above studies, average thickness of the deposit was 15-20 µm. The average thickness of the deposits was confirmed using SEM cross sectional photomicrographs.

Ferroxyl test was widely adopted to test the porosity in the deposit. Mild steel panels (7.5 × 7.5 cm^2) were used for the test. The porosity of each deposit was evaluated on the basis of number of blue spots formed[18].

In order to assess the stability of the bath solution, current efficiency and throwing power were measured at different current densities. A rectangular methacrylate cell of 250 mL capacity was used for the current efficiency measurement. An equal area of (4 × 4 cm^2)

cathode and anode were used for the current efficiency measurements. Electrodeposition was carried out for 10 min in each case[19].

Throwing power (TP) was measured in a Haring-Blum Perspex cell with an inside dimension $10 \times 4 \times 5$ cm^3. A porous zinc anode was placed between two plane parallel steel cathodes filling the rectangular cell cross section. One of the cathodes was nearer to anode than the other. The distance ratio was 5 : 1. The percentage of the throwing power was calculated from Field's formula[20].

Electrochemical experiments were carried out using an Electroanalyser (Model: EA-201, ChemiLink, Mumbai, India) coupled to a personal computer equipped with soft ware for data acquition. Polarization and voltammetric experiments were performed using a single compartment three-electrode cell with 100 mL capacity.

Linear polarization measurements were carried out in an aqueous 3.5 wt. % NaCl solution using mild steel as working electrode (0.125 cm^2), platinum as counter electrode and saturated calomel as reference electrode. Linear polarization measurements were performed by sweeping the potential between -200 to -2200 mV vs SCE at the scan rate of 10 mV/s. The corrosion potential (E_{corr}) and corrosion current (i_{corr}) were obtained using Tafel extrapolation method[21].

Cyclic voltammetric and cathodic polarization studies were carried out using glassy carbon (0.07 cm^2), platinum rod and saturated calomel as the working, counter and reference electrode, respectively. Prior to each experiment, the working electrode was polished to a mirror finish using alumina 0.05 μm (Buehler). After polishing, the electrodes were electrochemically pretreated in a solution containing 0.01 M K_4 [Fe (CN)]$_6$ and 1 M KNO_3. This pretreatment gives a better electrochemical response and assures reproducibility. The temperature of the cell was kept at 30°C.

The surface morphology of the electrodeposits with and without additive was observed using high resolution scanning electron microscopy (PHILIPS XL20). SEM images of the electrodeposits before and after electrochemical and chemical studies were taken to assess the morphology of the deposit (model JEOL-JSM-35 LF at 25 kV).

Salt spray test was carried out in accordance with ASTM B 117 specifications. The electrodeposited steel samples of 5×5 cm^2 area under different experimental conditions were taken for this study[22]. The specimens were carefully observed for every 24 h and the time taken for the formation of white rust was recorded.

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 Cu-K_α 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[23].

RESULTS AND DISCUSSION

Hull cell studies

Effect of additives

The basic bath solution gave coarse dull deposit in the current density range 1-10 A/dm^2 at 2A cell current. To improve the nature of the deposit, small amount of CTAB (surfactant) and condensation product of GGL and VNL was added to the bath solution. As a general effect, this additive smoothen the deposit and refined the grain size. Additives frequently assumed to act as catalysts or inhibitors in the electrodeposition process by increasing the tendency of metal ions to form complexes and/or raising the activation polarization of single ions by blocking the active sites on substrate[24]. According to the Hull cell results, the appropriate concentration of additive in plating bath to get mirror bright deposit was 30 ml/L. At this concentration, Hull cell panels were bright in the current density range of 1-10 A/dm^2.

Effect of zinc sulphate

To find out the effect of zinc sulphate concentration on the deposit nature, zinc sulphate concentration was varied from 50-300 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 1-10 A/dm^2.

Effect of sodium sulphate

To increase the conductivity of the bath solution, certain conducting salts having chloride and sulphate ions were used. 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 1-10 A/dm^2.

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[25,26].

To see the optimum concentration of boric acid, the concentration was varied from 10-50 g/L keeping the concentrations of zinc sulphate and sodium sulphate at 240 g/L and 40 g/L, respectively. At a concentration of 30 g/L, mirror bright deposit in the current density range 1-10 A/dm^2 was obtained. The concentration of boric acid was fixed at 30 g/L as optimum in the bath solution.

Effect of cetyl trimethyl ammonium bromide (CTAB)

The surfactants exhibit complexing property towards metal ions and thereby, controls 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[27]. The concentration of CTAB was varied from 1-4 g/L. At a concentration of 2 g/L, satisfactory bright deposits was obtained in the current density range of 1-10 A/dm^2 at 2A cell current.

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 and throwing power[18]. The Hull cell experiments showed that at a pH of 3, the cathodes were bright in the current range 1-10 A/dm^2 at 2A cell current. At high pH (>3), the cathode was covered with burnt deposit at high current density region and at low pH (<3) suffered from uncoated area at low current density region.

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[18].

Effect of current density

The Hull cell experiments were carried out at different cell currents (1-4A) for 10 min using optimized bath solution. At a cell current of 1A, the deposit was bright in the current density range of 0.5-5 A/dm^2. At 2A cell current, the deposit was bright in the current density range of 1-10 A/dm^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[18]. Based on the above observation bright current density was found to be 1-10 A/dm^2.

Current efficiency and throwing power studies

Current efficiency and throwing power were measured at different current densities by using optimized bath solution. At a current density of 2 A/dm^2, the current efficiency was found to be 96% and at 4 A/dm^2, it was 98%. With increase in the current density above 6 A/dm^2, the current efficiency was found to be decreased and at 10 A/dm^2, it was 90%.

However, increasing the current density from 2-10 A/dm^2, the throwing power of the bath solution was increased in the beginning from 24% to 28% at 4 A/dm^2. After that throwing power was decreased from 28% to 16%, as a result of increased polarization. The variation of throwing power and current efficiency with current density at pH 3 is given in Table 2.

Table 2: Current efficiency and throwing power of bath solution in presence of CTAB and condensation product

Current density (A/dm^2)	Current efficiency (%)	Throwing power (%)
2	96	24
4	98	28
6	93	21
8	92	19
10	90	16

Polarization studies

The polarization curves showed that the presence of condensation product in the bath solution shifts the cathodic potential to more negative values (Fig. 1). Generally, electroactive functional groups of the condensation product will adsorb at the electrode surface and reduce the surface stress at the gas-electrolyte interface and hence, shift of potential to more negative direction.

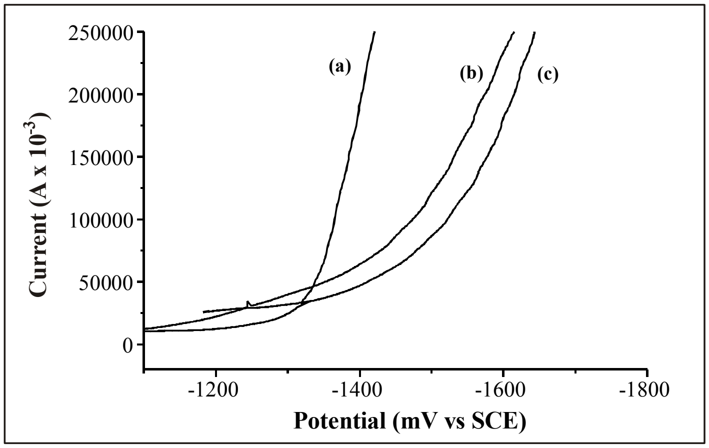

Fig. 1: Cathodic polarization curves for (a) basic bath (b) basic bath + CTAB and (c) optimum bath solutions.

Corrosion resistance studies

Fig. 2 present the effect of additive on corrosion behavior of zinc deposits in 3.5% NaCl solution. The negative shift in the E_{corr} confirms the good protection of mild steel when its surface covered by condensation product. Also, the Tafel measurements clearly show that substantial reduction in the corrosion current density (I_{corr}) occurs for the zinc deposit obtained in presence of addition agents. Hence, the deposit obtained in the presence of condensation product showed maximum corrosion resistance.

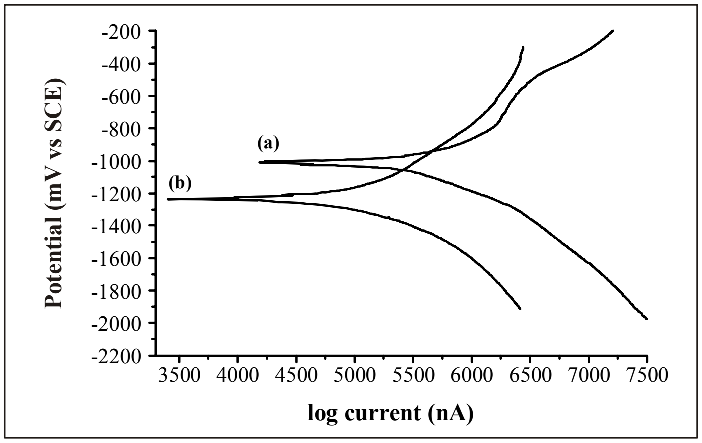

Fig. 2: Linear polarization curves for the zinc deposits obtained from (a) basic bath and (b) optimum bath solutions in 3.5 wt. % NaCl solution

Fig. 3 shows the cyclic voltammograms of the electrodeposited zinc in presence and absence of addition agents. It can be seen that the surface of the optimized zinc deposit is sufficiently smooth, and its free corrosion potential is more negative than pure zinc coating in the cathodic branch of the voltammograms, which indicates that the optimized zinc deposit is an ideal cathodic protective coating for mild steel, when compared to pure zinc coating.

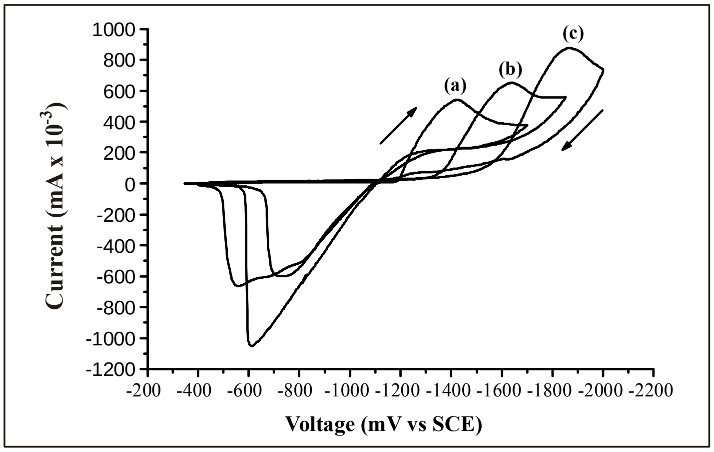

Fig. 3: Cyclic voltammograms for (a) basic bath; (b) basic bath + CTAB and (c) optimum bath solutions

Salt-spray test

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. This confirmed the enhancement of corrosion resistance of zinc in presence of condensation product.

Surface morphology studies

The nature of crystal growth in the presence and absence of condensation product is explained with the help of SEM photomicrographs as shown in Fig. 4. Fig. 4(a) is the SEM photomicrograph of the deposit obtained from the basic bath, which shows coarse-grained deposit having irregular crystal size. The deposit obtained from the optimized bath shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence, bright deposit [Fig. 4(b)].

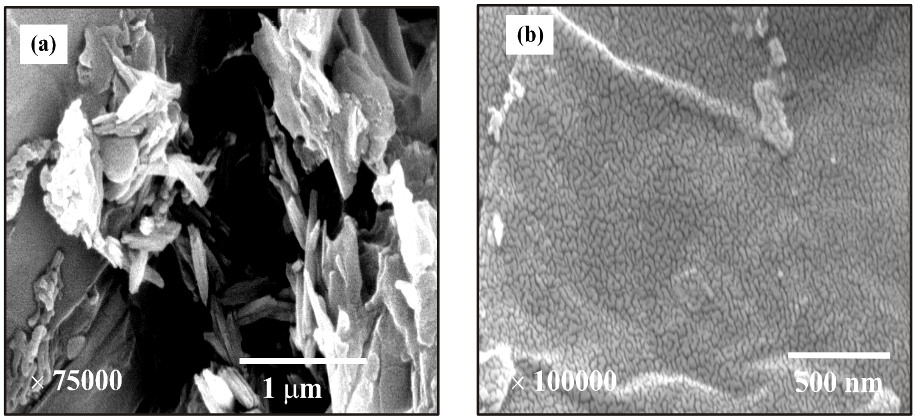

Fig. 4: High resolution SEM photomicrographs of the deposits obtained at 4 A/dm^2: (a) basic bath and (b) optimum bath solutions at 298 K

The zinc deposits obtained from the bath solution 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 mild steel obtained from basic bath Fig. 5(a). Very little corrosion is observed on the zinc deposits coated in presence of condensation product [Fig. 5(b)]. Fig. 6 shows the SEM images of zinc deposits with and without additive after potentiodynamic polarization in 3.5% NaCl solution. The SEM studies indicated that the deposits obtained in presence of additive showed higher corrosion resistance and the similar results were obtained by weight-loss and electrochemical measurements. Fig. 7 shows the SEM photomicrographs of cross section of zinc deposits with and without additive at a coating thickness 15-20 μm.

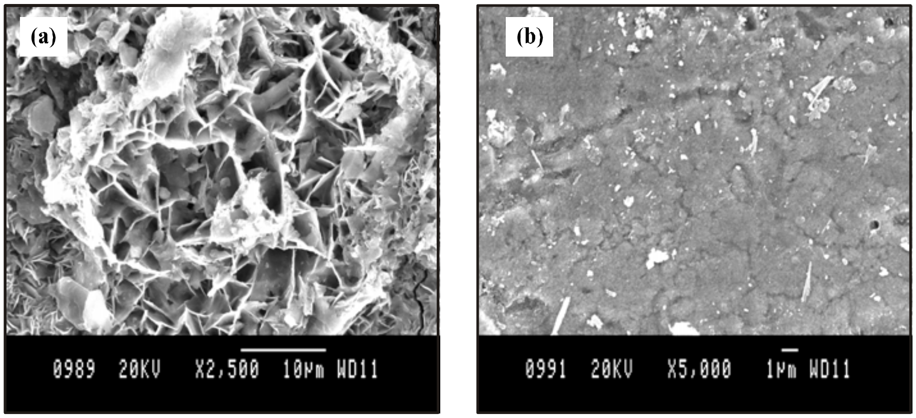

Fig. 5: SEM photomicrographs of the zinc deposits: (a) basic bath and (b) optimum bath solutions after 15 days of immersion in 3.5 wt. % NaCl solution.

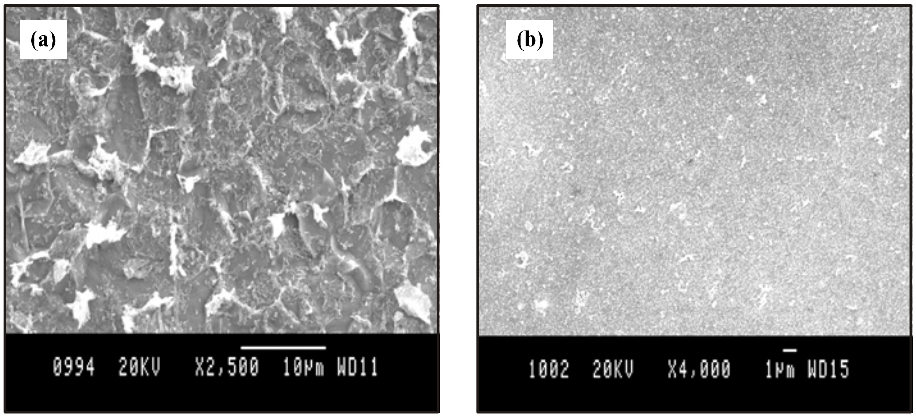

Fig. 6: SEM photomicrographs of the zinc deposits: (a) basic bath and (b) optimum bath solutions after potentiodynamic polarization in 3.5 wt. % NaCl solution03

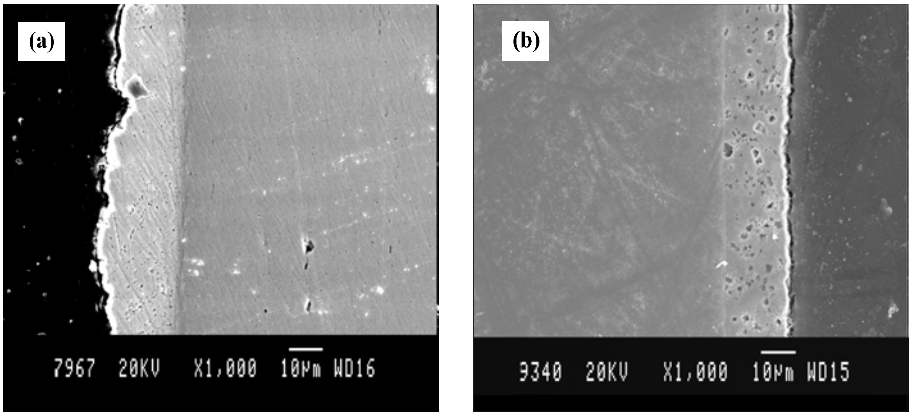

Fig. 7: SEM cross sectional photomicrographs of the zinc deposits: (a) basic bath and (b) optimum bath solutions

Adhesion and porosity studies

Standard bend test was adopted to measure both adherence and ductility of the zinc deposits. The deposited samples were subjected to bending 90° and then to 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 mild steel substrate.

Mild steel panels (7.5 × 7.5 cm^2) were used for the porosity test. The specimens obtained from basic bath showed very few blue spots at a thickness of 20 μm. But the deposits obtained from optimized bath did not show any blue spots. This indicated good surface coverage in the presence of brightener.

X-ray diffraction studies

Fig. 8 and 9 show X-ray diffraction patterns of the zinc electrodeposits obtained from the basic and optimized bath, respectively. The observed '2θ' value is in good agreement with the standard values for zinc deposition (Joint Committee on Powder Diffraction System (JCPDS)/ASTM File No. 1* 40831 Zn). 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 3. 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 18 nm and 68 nm, respectively.

Table 3: Parameters derived from XRD data

Bath system	**Average crystal size (nm)**	**2θ**		**hkl**
		Observed	**Standard**	
Basic bath	37.5	36.153	36.29	(002)
	83.43	38.8	38.9	(100)
	44.8	43.09	43.23	(101)
	84.5	54.3	54.3	(102)
	72.3	70.1	70.07	(110)
	76.97	81.9	82.0	(112)
	78.54	86.54	86.4	(201)
Optimum bath	15.28	38.4	38.99	(100)
	21.58	41.08	43.22	(101)
	25.14	45.32	43.22	(101)
	22.72	56.57	54.3	(102)
	11.25	72.45	70.6	(110)
	23.82	84.17	82.08	(112)
	23.38	88.5	86.5	(201)

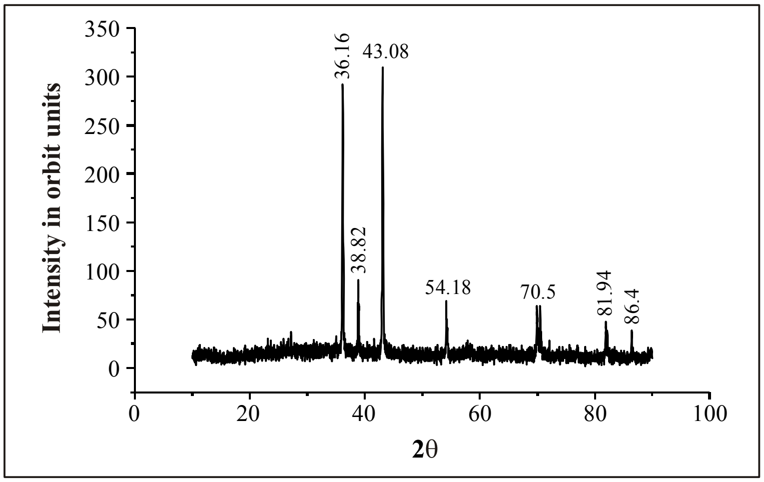

Fig. 8: X-Ray diffraction pattern of the zinc deposit obtained from basic bath solution

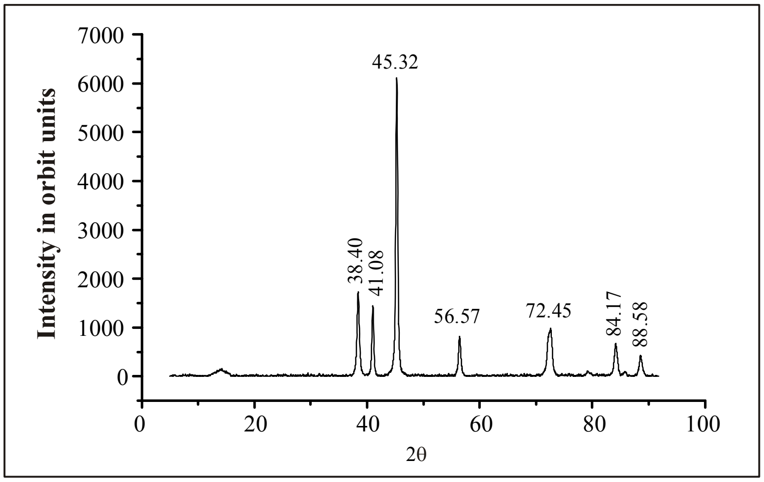

Fig. 9: X-Ray diffraction pattern of the zinc deposit obtained from optimum bath solution

CONCLUSION

A nanocrystalline zinc was electrodeposited on mild steel from simple acid sulphate bath. Developed bath is capable of producing good deposit over a current density range of 1-10 A/dm^2. The addition agent is a nontoxic simple water soluble condensation product of GGL and VNL. The current efficiency and throwing power of the developed bath were in the range of 90-98% and 16-28%, respectively. SEM and electrochemical measurements revealed the good corrosion inhibition of zinc coatings. XRD data confirmed the formation of nanocrystalline zinc coatings in presence of condensation product. In our view, the present bath with minor modifications can be used for commercial plating applications.

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