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Studies on nanocrystalline zinc coating

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Abstract. **Nano zinc coatings were deposited on mild steel by electrodeposition. The effect of additive on the morphology of crystal size on zinc deposit surface and corrosion properties were investigated. Corrosion tests were performed for dull zinc deposits and bright zinc deposits in aqueous NaCl solution (3·5 wt.%) using electrochemical measurements. The results showed that addition of additive in the deposition process of zinc significantly increased the corrosion resistance. The surface morphology of the zinc deposits was studied by scanning electron microscopy (SEM). The preferred orientation and average size of the zinc electrodeposited particles were obtained by X-ray diffraction analysis. The particles size was also characterized by TEM analysis.**

Keywords. **Electrochemical deposition; glycyl–glycine; sulphate bath; zinc coating.**

1. Introduction

Metals at the nanometer scale exhibit unusual behaviour compared to their bulk counterparts (Cheung *et al* 1996; Erb *et al* 1996; Tellkamp and Lavernia 1999). Such unusual properties have generated interest in nanostructured materials for corrosion and wear resistance coatings, soft magnetic materials for magnetic recording, and electrocatalyst for hydrogen evolution and oxidation reactions (Inturi and Szklarska-Smialowska 1992).

These nanostructured materials can be synthesized by a number of techniques such as arc discharge, laser ablations, CVD (chemical vapour deposition), PVD (physical vapour deposition), VLS (vapour liquid solid), SLS (solid liquid solid), and seed mediated growth are important. Although the use of many such techniques is limited to laboratory scale, inert gas condensation, mechanical alloying, and electrodeposition are among the methods that are available for commercial use (Suryanarayana 1995). Electrodeposition can lead to easy control of thickness and low cost of production compared with the conventional rolling process. Moreover, deposited films having nano-size grains were reported to enhance the properties such as electrical resistivity, hardness, corrosion and wear resistance (Zener 1951). So, electrodeposition method is applied as a new invar fabricating process and deposition condition to control the grain size and this is focused in our research (Anderson and Hasegawa 1955).

The grain size of the electrodeposits depends on the deposition parameters such as pH of the electrolyte (Ebrahimi *et al* 1998), deposition technique (Ebrahimi *et al* 1999), current density (Morgan *et al* 2001) and substrate (Ebrahimi and Li 2003), as well as on the type and amount of additives included in the electrolyte (Ebrahimi and Ahmed 2003). The addition of organic compounds to the electrolytic baths can modify deposit characteristics such as structure, morphology, porosity and grain size (Ei-Sherrik and Erb 1995; Arthoba Naik *et al* 2000, 2001; Arthoba Naik and Venkatesha 2005).

In the present work, the effect of condensation product on the crystal structure of the electrodeposited zinc was investigated with XRD, SEM and TEM analyses.

2. Experimental

All the solutions were prepared from AR grade chemicals and double-distilled water. To judge the quality and nature of the zinc deposits from the zincate electrolytes at various current density, pH and temperature, plating was carried out on polished mild steel sheets using standard 267-ml Hull cell for 10 min. The optimum concentration of condensation product was also determined by using Hull cell tests at various concentrations while keeping the other parameters constant in each case. The Hull cell experiments with the bath solutions given in table 1 were carried out without agitation. The pH of the 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. The anode was 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 mechani-

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Table 1. Optimum bath composition and operating conditions.

Bath composition	Quantity (gL^{-1})	Operating conditions
$ZnSO_4 \cdot 7H_2O$	240	Anode: Zinc metal (99·99%)
Na_2SO_4	40	Cathode: Mild steel
H_3BO_3	40	Temperature: 293–303 K
CTAB	2	Current density: 1–6 Adm^{-2}
Condensation product (GGL–FFL) (mLL^{-1})	80	

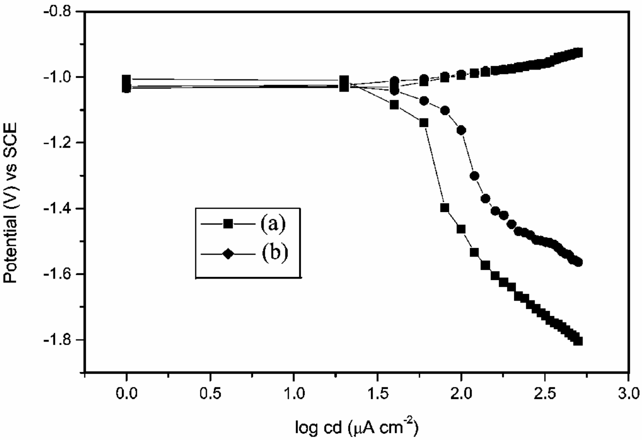

Figure 1. Potentiodynamic polarization curve for coating thickness, 7·5 μm, in 3·5 wt.% NaCl solution: (a) dull zinc deposit and (b) bright zinc deposit.

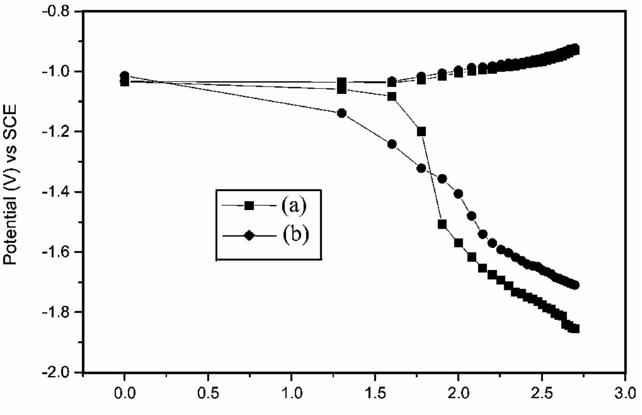

Figure 2. Potentiodynamic polarization curve for coating thickness, 15 μm, in 3·5 wt.% NaCl solution: (a) dull zinc deposit and (b) bright zinc deposit.

cally polished 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 were subjected to electrocleaning process. The thickness of the deposited layer has been approximately estimated from the procedure given elsewhere (Ohtsuka *et al* 1995; Abou-Krisha 2005).

Table 2. Galvanostatic polarization in 3·5 wt.% NaCl solution.

Bath system	Deposit thickness (μm)	E_{corr} (−mV vs SCE)	i_{corr} (A cm^{-2})
Dull zinc deposit	7·5	1040	35·48
Bright zinc deposit		1020	17·78
Dull zinc deposit	15	1035	31·62
Bright zinc deposit		1100	19·95

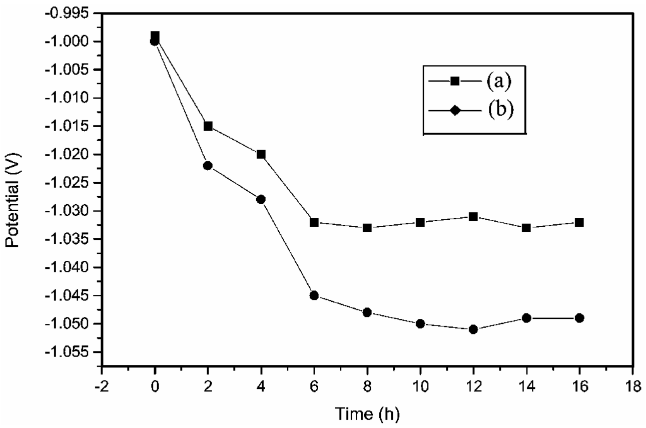

Figure 3. Variation of the corrosion potential (E_{corr}) with immersion time for zinc coated samples in 3·5 wt.% NaCl solution: (a) dull zinc deposit and (b) bright zinc deposit.

The additive was synthesized by using the procedure given elsewhere (Muralidhara *et al* 2006). 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.

The effect of condensation product on corrosion resistance of the zinc deposits was studied in 3·5 wt.% NaCl solution by galvanostatic polarization method. A three-electrode cell assembly was used. The working electrode (WE) was masked with lacquer to expose 1 × 1 cm^2 area. A platinum foil was used as the counter electrode (CE) with saturated calomel as reference electrode (RE). The polarization behaviour was studied in the test electrolyte for zinc deposit of different thicknesses (7·5, 15 μm). The working electrode was cleaned and kept in a 3·5 wt.% NaCl solution for 20 min to establish a steady state poten-

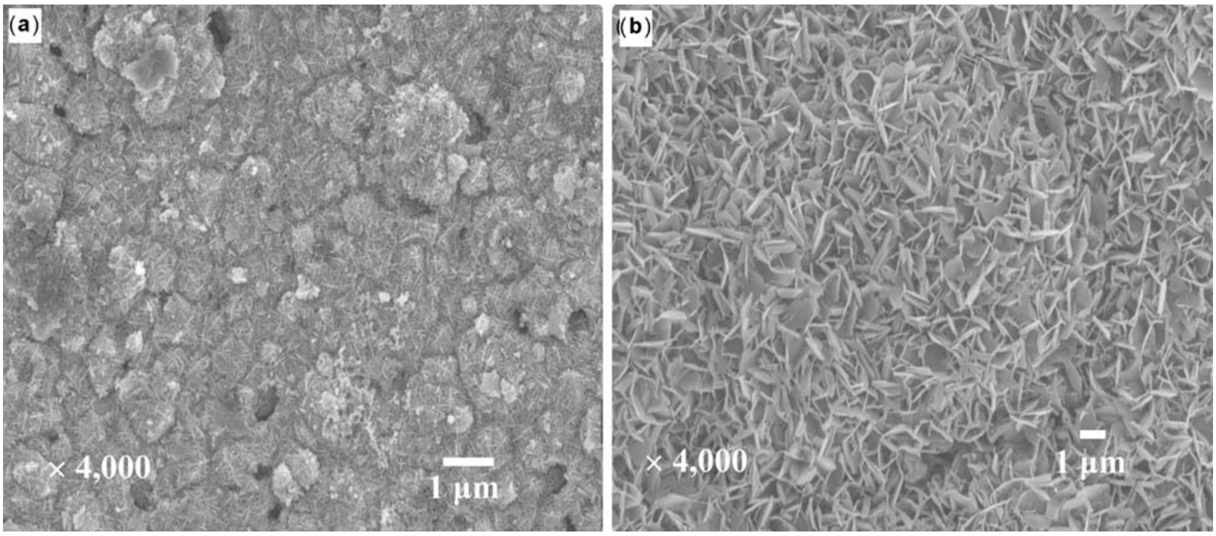

Figure 4. SEM photomicrographs of the deposits obtained at 3 Adm^{-2}: (**a**) dull zinc deposit and (**b**) bright zinc deposit.

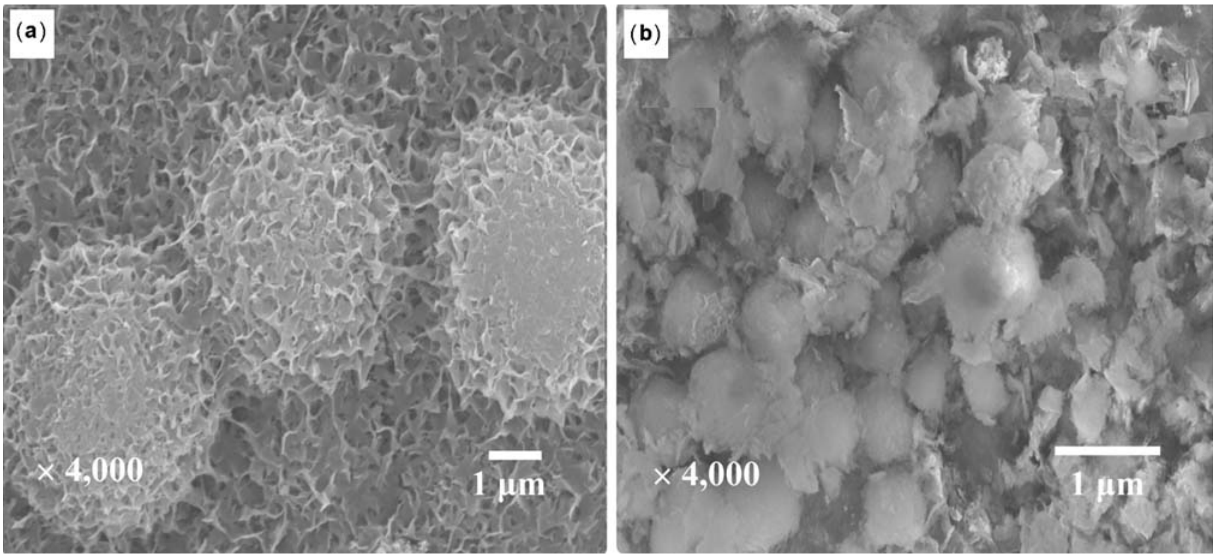

Figure 5. SEM photomicrographs of the deposits after 15 days immersion in 3·5 wt.% NaCl: (**a**) dull zinc deposit and (**b**) bright zinc deposit.

tial. 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. Corrosion potential (E_{corr}) and corrosion current (i_{corr}) values were obtained by Tafel extrapolation method from the plot of E vs $\log i$ curves (Senthil Kumar *et al* 2001).

The variation of OCP of steel deposited samples with and without additive were measured in a solution of 3·5 wt.% NaCl as a function of time at 298 K. The exposed area of the specimen was 3×4 cm^2. The corrosion potentials were measured for every 30 min interval for a period of 15 h.

Corrosion test was carried out in a salt spray chamber at 25 ± 2°C, in accordance with the ASTM B117 method. All coatings were 15 μm thick. Some of the coatings were chromated with iridescent yellow chromate (Arthoba Naik 2002) for 5–20 s. For every 24 h, the samples were examined for the formation of white rust.

The surface morphology study of coated samples, before and after corrosion tests, was observed using JEOL-JSM-35 LF scanning electron microscopy (SEM).

X-ray diffraction studies of the zinc deposits were carried out by using Philips TW 3710 X-ray recorder. Nickel-filtered Cu-Kα radiation was used to determine the lattice parameter, crystallographic texture and approximate average

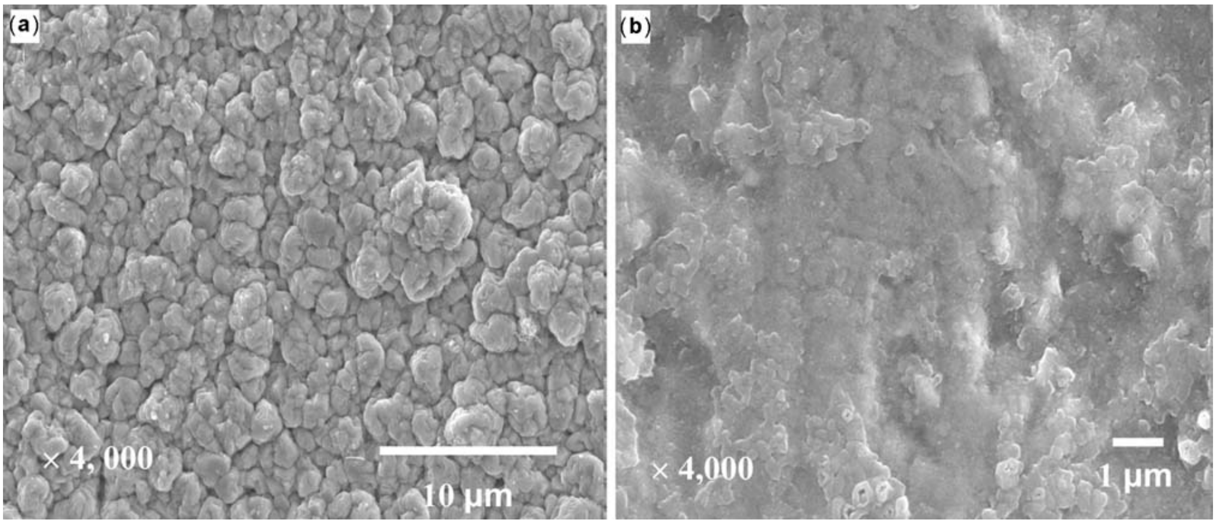

Figure 6. SEM photomicrographs of the deposits after cathodic polarization: (**a**) dull zinc deposit and (**b**) bright zinc deposit.

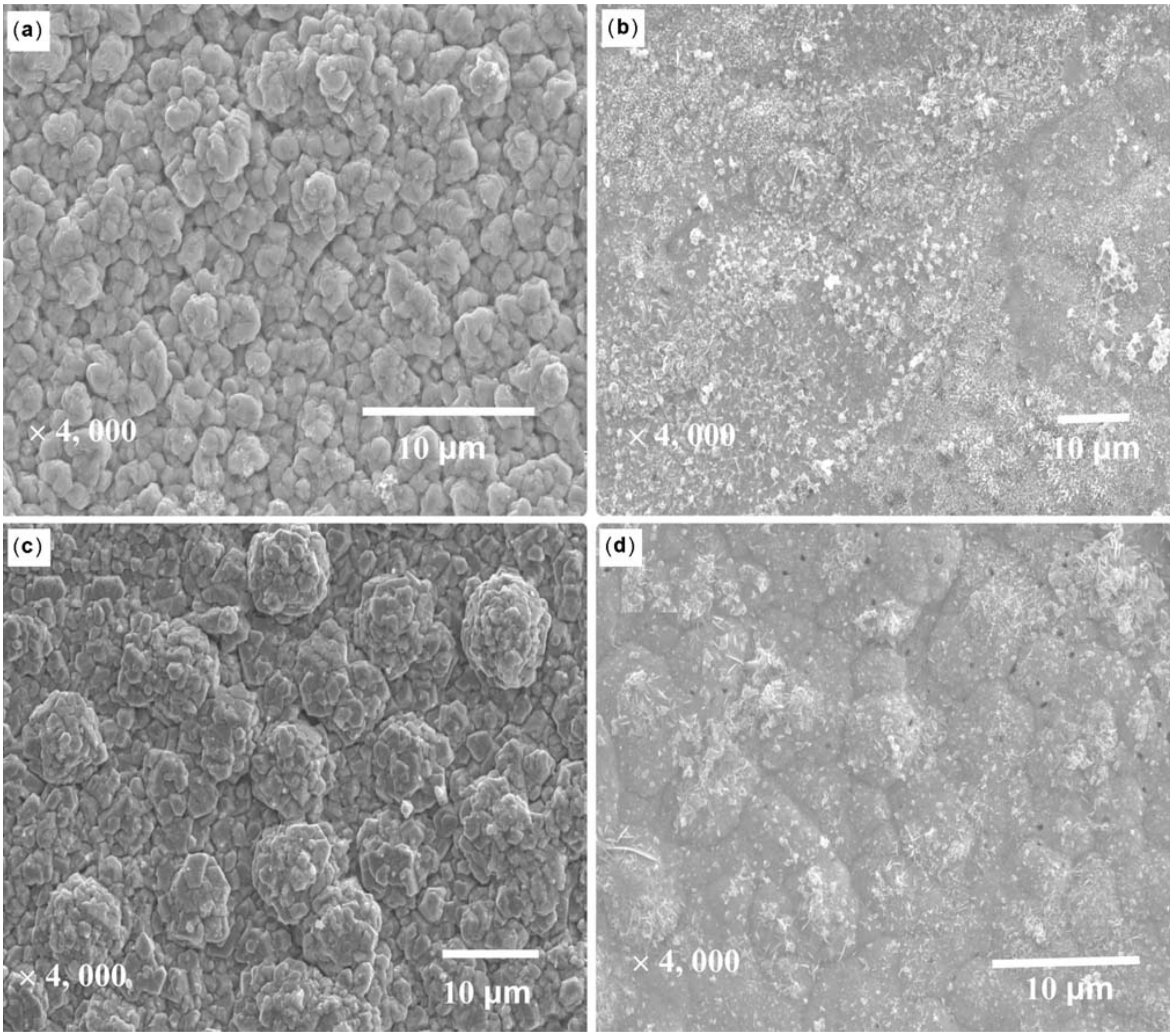

Figure 7. SEM images of the samples of coating thicknesses, 7·5 µm and 15 µm, after potentiodynamic polarization: (**a**, **c**) dull zinc deposits and (**b**, **d**) bright zinc deposits.

grain size of the deposit. The grain-sizes of the coating were calculated using Scherrer's equation (Juarez and Alonso 2003).

TEM was performed using JEOL/JEM-200 LR equipped with a field emission gun. An accelerating voltage of 200 kV was used.

3. Results and discussion

3.1 *Corrosion resistance studies*

Figures 1 and 2 present the effect of additives on corrosion behaviour of zinc deposits of 7·5 and 15 μm thickness in 3·5 wt.% NaCl solution. The polarization values are given in table 2. From the figures it can be seen that the i_{corr} values for bright zinc deposits were considerably lower indicating a reduction in the metal dissolution rate. Hence the deposit obtained from the optimized bath showed maximum corrosion resistance.

3.2 *OCP measurement*

The plots of OCP vs time for zinc deposits are shown in figure 3. From the figure it is clear that the presence of condensation product shifted the OCP value to the negative direction. This indicates that added condensation product forms the passive layer on the zinc coated surface and thereby protecting the mild steel.

3.3 *Salt-spray studies*

Salt spray test has probably received more attention than any other laboratory corrosion tests for electroplated zinc coatings, since it is an accelerated corrosion test. In principle, it consists of exposing the test specimen to a controlled fog (mist) of a reagent solution (depending on the type of coating) and observing the condition of the specimen after specified number of treatment hours. The number of hours for the formation of white rust was the indication of the corrosion resistance. The higher corrosion resistance delays the production of white rust. In the present case, dull zinc deposit produced white rust after 24 h and the bright deposit produced white rust after 96 h. Chromate passivated sample did not show white rust even after 96 h of testing. This test confirms the enhancement of corrosion resistance of zinc in presence of the additives.

3.4 *Surface morphology studies*

The nature of crystal growth in the presence and absence of addition agents is explained with the help of SEM photomicrographs (figure 4). In figure 4(a), the crystal growth is not uniform, the basic bath produced deposit having slightly larger crystal sizes. SEM photomicrograph of the optimized bath showed a uniform arrangement of crystals, refinement in the crystal size and hence gave bright and corrosion resistance deposit (figure 4(b)).

Figure 5 shows the surface morphology of dull and bright zinc deposits after treatment with 3·5 wt.% NaCl solution for 15 days. The dull deposit obtained from basic bath shows serious corrosion attack of the aggressive medium (figure 5(a)). The corrosion surface of bright zinc coating, shown in figure 5(b), shows relatively less corrosion products indicating the stability of bright zinc deposit towards corrosion inhibition. This may be attributed to the presence of passive layer of additive on the surface of the deposit. Figures 6(a) and (b) represent the SEM images of dull zinc and bright zinc, respectively after cathodic polarization in 3·5 wt.% NaCl solution. Large differences

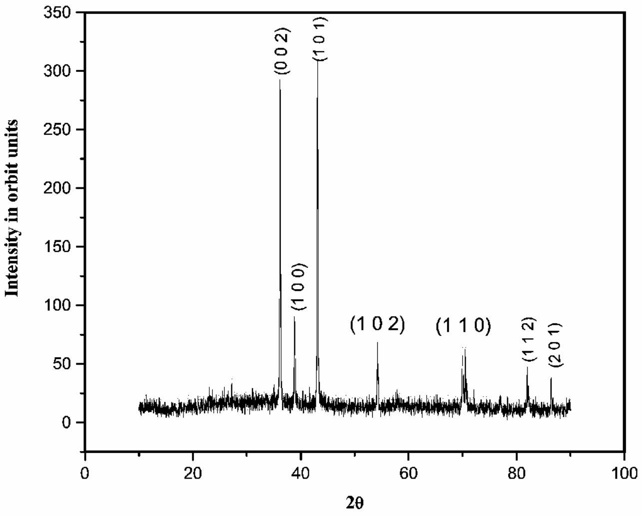

Figure 8. X-ray diffraction pattern of the dull zinc deposit.

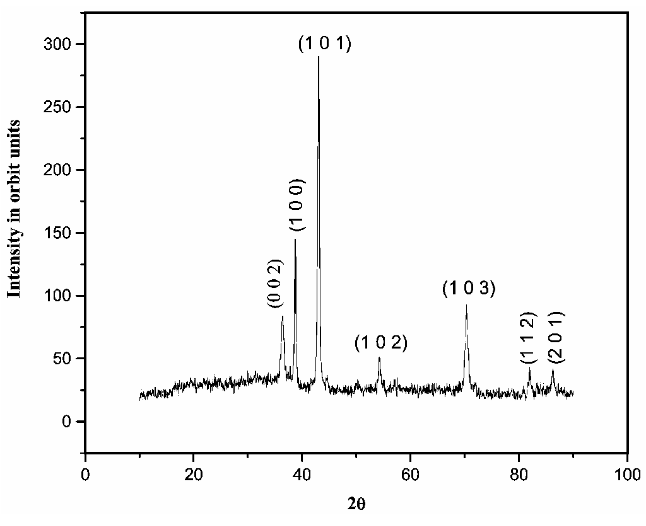

Figure 9. X-ray diffraction pattern of the bright zinc deposit.

Table 3. Parameters derived from XRD data.

Bath system	Average crystal size (nm)	2θ Observed	2θ Standard	*hkl*
Dull zinc deposit	46·88	36·17	36·29	(0 0 2)
	44·8	43·11	43·23	(1 0 1)
	91·66	86·39	86·55	(2 0 1)
Bright zinc deposit	12·91	36·43	36·29	(0 0 2)
	21·50	43·03	43·23	(1 0 1)
	20·17	86·27	86·55	(1 0 1)

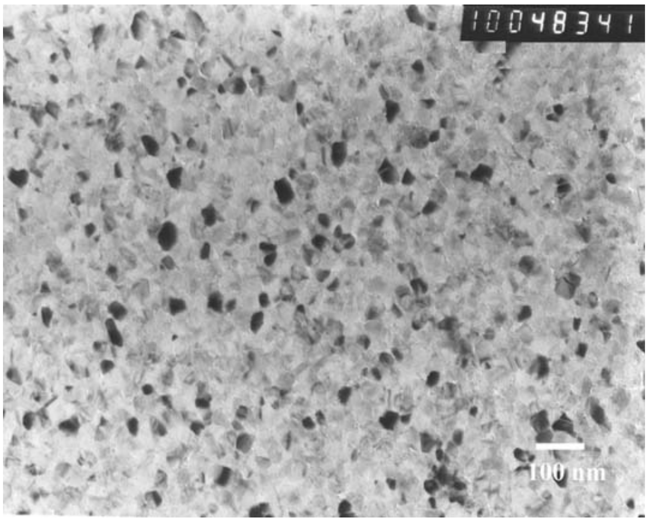

Figure 10. TEM image of the bright zinc deposit.

can be observed in the corrosion pattern of the deposits. The attack of corrosive medium on dull deposit was found to be more rapid than on the bright zinc deposit. SEM images of coated steel samples of 7·5 and 15 μm thickness after potentiodynamic polarization in 3·5 wt.% NaCl solution is shown in figure 7. Figures 7(a) and (b) are the SEM photomicrographs of dull and bright zinc deposited specimens with a coating thickness of 7·5 μm. Figures 7(c) and (d) are the SEM photomicrographs of dull and bright zinc deposited specimens with a coating thickness of 15 μm. These studies indicated that the deposit obtained in presence of condensation product showed higher corrosion resistance.

3.5 *X-ray diffraction studies*

The crystal structures of the zinc coatings with and without additive were investigated by using X-ray diffraction technique. The 2θ values of the sample match well with the standard JCPDS file. Figures 8 and 9 show typical X-ray diffraction patterns of dull and bright zinc deposit, respectively. Crystalline size was determined from the full width at half maximum (FWHM) of the X-ray peaks present on the diffractogram and corresponding results are given in table 3. The X-ray patterns of the bright deposit showed a broadening of the diffraction peaks. This broadening can be attributed to the refinement in grain size. The average grain size of crystallites from dull deposit was 61 nm and it was 18 nm for bright deposit.

3.6 *TEM studies*

Figure 10 shows TEM photomicrograph of bright zinc deposit. The particles of the deposit obtained in presence of additive has an average grain size of 15 nm. This confirmed the role of addition agent on crystal growth in morphology of zinc coating surface by refining the microstructure.

4. Conclusions

Electrodeposition is a versatile technique for producing nanocrystalline zinc deposition. The deposition of zinc from sulphate baths showed higher conductivity, low cost and non-polluting nature. The use of additives in an electrolytic bath changes the morphology of zinc coating surface by refining in the microstructure. Electrochemical measurements and SEM analysis confirmed that bright deposits showed higher corrosion resistance than dull zinc coatings. XRD and TEM analysis confirmed the formation of nanocrystalline zinc deposition.

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