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Synergistic effects of additives on morphology, texture and discharge mechanism of zinc during electrodeposition

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The effect of different combination of additives, cetyltrimethylammonium bromide (CTAB), salicylaldehyde (SAL) and acetic acid (AA) on surface morphology, texture and grain size of zinc electrodeposits were systematically analyzed by scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD). Results show that, the co-existence of all three additives in plating bath generates uniform, compact and bright zinc deposit. The voltammetric studies reveal the combined interaction of additives on plating surface during electrodeposition. This interaction leads to synergistic effect on smoothening the deposit surface, refining the grain size and development of the preferred orientation of the deposit. Also influence of additives on nucleation and growth mechanisms of zinc at glassy carbon electrode were investigated by chronoamperometric studies.

1. Introduction

Electrodeposition of zinc on steel is the most widely used industrial surface finishing process as it sacrificially protect steel against corrosion at low cost. For zinc plating wide varieties of plating baths have been cited in the literature and are employed on industrial scale. The primary requirement of these baths is to produce smooth, compact, bright deposit of improved properties over large range, 1–100 A cm^{-2} of current densities. These properties depend on the nature and concentrations of bath constituents. The main constituents of bath are metal ions, conducting salts, buffers and addition agents. Among these only the addition agents play a prominent role in producing bright deposit of improved quality [1–3]. The commonly used additives in electroplating baths are classified as levelers and brighteners [4–6]. The brighteners are organic compounds usually added in small quantity (10^{-4}–10^{-2} M) to the bath solution. The deposit obtained in their presence exhibit improved material properties such as surface reflectance, and corrosion resistance. The carbonyl compounds like o-chlorobenzylaldehyde [5], benzylideneacetone [7–13], Vanilline [14] glycyl–glycine [2] etc. were reported as brighteners for zinc deposition.

The levelers are generally used in relatively higher concentrations around 10^{-2} M. They smoothens the deposit surface [15]. The surfactants like CTAB (cetyltrimethylammonium bromide), SDS (sodium dodecylsulfate), polyethylene glycol (PEG) and Triton X-100 were used as levelers for zinc electroplating [16–20]. Surfactant refines the grain size of deposit, microscopically smoothens the deposit surface, improves throwing power and solubility of brighteners in bath solution [9,21]. Some additives simultaneously act as levelers and brighteners. But in most cases, combinations of different additives gave satisfactory deposit. The suitable combination of two or more additives improves the appearance and corrosion resistance of deposit as well as the throwing power and current efficiency of the bath solution compare to single additive [23–25].

The most important influence of additives on zinc electrodeposition are, (a) Morphological and microstructural changes: refinement of grain size [6,15] of deposit and formation of oriented grain structure [22] and (b) Electrochemical change (current – potential relations for zinc reduction).

Few researchers in their work considered synergistic interaction between the additives, to explain their role in producing bright or quality deposit [7,22,26]. Hsieh et al. reported the existence of complicated interaction among additives NP16 (polyoxyethylene nonyl phenyl ether), OCBA (o-chloro benzyl aldehyde) and S40 (polyoxyethylene lauryl amine). This interaction exhibits synergistic effect on smoothening zinc deposit and increasing current efficiency at high current density region (HCD) [5]. In another study [27], Hsieh et al. also investigated zinc deposition from baths containing polyamines: polyethyleneimine (PEI, Lugalvan G35) or the reaction product of imidazole and epihalohydrin (Lugalvan IZE) or polyquaternary amine salt (Lugalvan P), in a HCD process. They also, showed that the charge density of additives is an important

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Table 1
Plating bath composition.

Components (M)	Bath				
	I	II	III	IV	V Optimized bath
$ZnSO_4{\cdot}7H_2O$	0.55	0.55	0.55	0.55	0.55
Na_2SO_4	1.5	1.5	1.5	1.5	1.5
H_3BO_3	0.13	0.13	0.13	0.13	0.13
CTAB	–	0.0038	0.0038	–	0.0038
SAL	–	–	0.0008	0.0008	0.0008
AA	–	–	–	0.035	0.035

parameter for producing a uniform, smooth, and compact HCD Zinc deposit. The adsorption strength of the additives decreased in the order: Lugalvan P > Lugalvan IZE > Lugalvan G35. A strong synergistic effect between quaternized pyridine carboxylic acid and ployamine additives significantly improves the morphology at HCD zinc deposits [28]. Li et al. reported synergistic interaction between additives thiourea and benzalacetone on refining the grain size of deposit. This additive combination increased the overpotential, nucleation rate and retarded the rate of growth of nuclei during electrodeposition [26]. Moucheng Li et al. in their work concluded that a bright zinc coating with grain size of 43 nm and the (1 1 0) (1 0 0) (2 0 1) preferred orientation is produced due to co-existence of all four compounds CTAB, PEG, benzalacetone and thiourea [21]. The existing reports reveal that zinc plating baths are associated with two or more addition agents and their effect on generating bright deposit is more pronounced when used in combination. Synergistic interaction always expected between additives when they are present together in plating bath. Hence the detail research is required to know the role of additives and their influence on the formation of good quality deposit.

The present work is focused to study the effect of additives such as cetyltrimethylammonium bromide (CTAB as surfactant) and salicylaldehyde + acetic acid (SAL + AA as brightener) mixture [29] on morphology, microstructure of deposit and the reduction of zinc ion at cathode. Also the combined influence of additives on nucleation and growth mechanism of zinc deposit is elucidated.

2. Experimental

The mild steel plates of 4 × 4 cm^2 area were polished mechanically, degreased with vapors of trichloroethylene and finally immersed in 10% HCl to remove dust and rust. These plates were transferred to plating bath after washing with running water. The anode was 99.9% zinc metal plate and its surface was activated each time by dipping in 10% HCl for few seconds and washed with water. The chemicals used were of analytical grade (s d-fine, Mumbai, India) and bath solutions were prepared in Millipore water (Elix 3, France). The composition of the bath solutions (with different combination of additives) used for zinc electrodeposition is given in Table 1. The bath solution consisting of zinc salt $ZnSO_4{\cdot}7H_2O$, conducting salt Na_2SO_4 (supporting electrolyte), buffering agent H_3BO_3 (maintain pH of bath solution) and additives at their optimum concentration (Hull cell studies). The pH of bath solutions was adjusted to 2.8 with 10% H_2SO_4 and $NaHCO_3$. The deposits were obtained on mild steel plates at 25 mA cm^{-2} current density for 20 min using DC power supply (pS-618 potentiostat/galvanostat).

The surface morphology of the deposits was analyzed by scanning electron microscopy (SEM, LE01530-VP). The preferred orientation and grain size of deposits were determined by X-ray diffraction analysis (PHILIPS-1710) using Cu Kα radiation ($\lambda = 1.54$ Å) at 40 kV. The measurements were performed at 2θ range 30–90°. The grain size was evaluated by Scherer's equation $D = k\lambda/\beta\cos\theta$, where, $k = 0.9$, β is full width at half maximum, θ is angle of reflectance and λ is wave length of radiations used [21]. The average crystal size of each deposits are given in Table 2. The total uncertainty in crystallite size is due to the curve fitting process used to determine the peak height and experimental variability. The total uncertainty in the crystallite size measurements for each deposit is provided in Table 2. The reflectance values of zinc deposit were recorded using NOVO gloss meter, referenced against a vacuum coated silver mirror. The reflectivity of silver mirror was set at 100% at an angle of 60°. The measurements were carried out at different points of the coating surface and the average value had been presented in Table 2.

Surface profiles of the electrodes were monitored using a Stylus profilometer (Talysurf Plus, Rank Taylor Hobson Ltd., U.K.). Five tracings at different locations on each specimen were made and the average value of roughness has been presented in Table 2.

The electrochemical studies were carried out using CHI660C electrochemical workstation USA in a conventional three electrode cell. The working electrode was glassy carbon disk of surface area 0.07065 cm^2 enclosed in Teflon tube. The surface of working electrode was prepared by polishing with 0.05 μm alumina, agitated ultrasonically for 15 min in 10% HCl and then washed with running water. The platinum wire and saturated calomel electrode (SCE) were employed as counter and reference electrodes respectively.

Electro-active surface area of glassy carbon electrode was determined to be 0.0693 cm^2 by using an aqueous solution of 10 mM $ZnSO_4{\cdot}7H_2O$ in 1 M KCl and diffusion coefficient, $D_{(1/2Zn^{2+})} = 7.03 \times 10^{-6}\ cm^2\ s^{-1}$ [30].

3. Results and discussion

3.1. Deposit morphology and orientation

The zinc deposits are obtained from bath solutions given in Table 1. The SEM images were recorded for each deposit plated at 25 mA cm^{-2} current density for 20 min and presented in Fig. 1. The SEM image of deposit obtained from bath-I show random distribution of nano-laminated thin hexagonal platelets (Fig. 1a). The surface roughness of the deposit is higher about 105 nm and large hexagonal platelets (1 μm) with thickness less than 0.1 μm are observed. The deposit is dull with reflectance of 7%. In presence of 0.0038 M CTAB (bath-II) the grain size of deposit is reduced and needle shaped crystals of uniform size (1 μm), were obtained (Fig. 1b). The deposit is porous, semi bright with reflectance of 27% [16] and surface roughness is reduces to 45 nm. Further the zinc deposit generated in presence of CTAB + SAL mixture, gave burnt non adherent deposit made up of loosely arranged thin hexagonal platelets (thickness ~0.1 μm) aligned perpendicular to the plating surface (Fig. 1c). But in presence of SAL + AA (bath-IV),

Table 2
Roughness, appearance, reflectance and grain size of deposit.

Bath	I	II	III	IV	V
Roughness (nm)	105	45	–	118	21
Appearance	dull	semi bright	Black	dull with black spot	Bright
Reflectance (%)	07	27	–	05	75
Grain size (nm)	156 ± 4	58 ± 2.2	49 ± 1.2	125 ± 3.5	57 ± 2.2