Research Article

A STUDY INTO THE ELECTRODEPOSITION OF BRIGHT ZINC ON MILD STEEL FROM ACID SULPHATE BATH

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ARTICLE INFO	ABSTRACT
	In the present work the electrodeposition of zinc from sulphate bath has been carried out in presence of a newly synthesized brightener, which is a condensation product of Cysteine Hydrochloride and Glutaraldehyde (CG). The cyclicvoltammetric and chronoamperometric techniques were used to study the nucleation mechanism involved in the electrodeposition process, while the polarization and electrochemical impedance spectroscopic techniques, were used for corrosion studies. The model of Scharifker and Hills was used to analyze the current transients and it revealed that the zinc electrocrystallization process, in presence of CG is regulated by instantaneous nucleation mechanism. The surface morphology of the deposit was characterised by Scanning Electron Microscope (SEM) and reflectance studies. The preferred orientation and crystallite size of the zinc electrodeposits were studied by X-ray diffraction analysis. These studies revealed the influence of CG in producing a bright coating and also exhibited higher corrosion resistant nature.

INTRODUCTION

Electrodeposition is a well-known conventional surface-modification method to improve the surface characteristics, both decorative and functional properties of a wide variety of materials. (Sobha 2012). Zinc is preferred for the electrodeposition process due to its relative ease of deposition and better corrosion resistance (Arthoba Naik. and Venkatesha T.V, 2005). Pure zinc deposition on steel is most extensively used for sacrificial anodic protection of iron or steel products against corrosion. The protection ability of zinc in aggressive environments is reduced due to sacrificial nature of zinc. Hence efforts are made to improve the consistency of zinc coating as an anti-corrosion material by adding additives in plating bath, which develop nanocrystalline bright zinc coating having comparatively better corrosion resistance property (Nayana *et al*., 2017).

The additives adsorbed on the cathode surface affect activation energy and the rate of charge transfer in the electrochemical reaction and may also influence the mechanism of crystallization (Basavanna S. and Arthoba Naik, 2011). This gives microstructural characteristic properties such as grain size, surface morphology and preferred orientation of coatings (Nayana *et al*., 2011; Youssef *et al*., 2004; Chen *et al*., 1999).

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This modification of surface morphology affects its corrosion resistance and other properties. The organic additives called brighteners are gaining attention as they not only give a decorative look but also improve the corrosion resistance ability of the electrodeposit. Most of the additives possess electroactive functional groups (Shivakumara *et al*.,2007) The condensation product of aldehyde and amine is acting as a good brightener than single aldehyde or amine in the bath solution due to the presence of – CH=N– group in the molecule (Kariyanna and Venkatesha, 2005; Kariyanna *et al*., 2003). Hence in the present work an attempt has been made to synthesize a new brightener by condensation of Cysteine Hydrochloride and Glutaraldehyde to increase corrosion resistance of bright zinc coating on mild steel.

Experimental

The nanocrystalline bright zinc coating was electrodeposited on mild steel by galvanostatic current control technique using acid sulphate bath. Similar to earlier studies the effect of bath constituents, pH, current density and temperature were optimized using a standard 267 ml Hull cell (Muralidhara *et al*., 2006; Muralidhara *et al*., 2008; Ganesh Achary *et al*.,2006; Basavanna and Arthoba Naik; 2012; Ganesh Achary *et al*.,2007) . The Hull cell experiments were carried out without agitation (Ganesh Achary *et al*., 2007) and the pH of solution was adjusted with 10% H_2SO_4 or sodium bicarbonate solution (Nayana and Venkatesha, 2014). All the chemicals were analytical grade and the solutions were prepared in distilled water. The experiments were conducted at room temperature

(298K). The anodic surface was activated each time by acid dip method in 10% HCl for 4-5s followed by washing with running water. The mild steel cathode surface was mechanically polished with emery paper and degreased with trichloroethene and then immersed in 10% HCl to remove the dust and rust. The plates were then washed with running water, dried and then transferred to plating bath solution for electrodeposition. After electrodeposition the adsorbed impurities on coated surface were removed by bright dip in 1% HNO_3 solution for 3-5s followed by water wash and dried (Basavanna and Arthoba Naik, 2012).

The condensation product was synthesized from equimolar amounts of cysteine hydrochloride (1mM) with chemical formula $C_3H_{10}ClNO_3S$ and Glutaraldehyde (1mM) with chemical formula $C_5H_8O_2$(AR grade, s d fine chemicals) in ethanol medium (50 ml) under reflux condition for 3 hrs at 343K (Chen and Martel,1987). The completion of the reaction was confirmed by thin layer chromatography (TLC).The resulting product was diluted to 100 ml with distilled water and a known amount of this solution was added to the plating bath solution. The bath solution was stirred for 30 minutes before conducting the experiments for proper mixing of condensation product with plating bath solution.

The cyclicvoltammetric and chronoamperometric studies were performed using CHI660D electrochemical workstation with a three electrode system. A graphite electrode of geometrical area 0.02 cm^2, a platinum wire and saturated calomel electrode were used as working, counter and reference electrodes respectively. Before conducting each experiment, the working electrode was polished to a mirror finish with 0.05μm alumina. The potentiodynamic polarization and electrochemical impedance studies were carried out in a typical three electrode cell with coated mild steel electrode (area 1 cm^2) as working electrode. The corrosion behaviour of zinc coatings obtained from plating bath in presence and absence of CG was measured in 3.5 wt % NaCl solution.

The surface morphology of deposits on mild steel electrodes was examined using scanning electron microscope (JEOL-JSM-6400). The Philips X'pert PRO MPD X-ray diffractometer was used to determine the orientation of zinc crystallites in the deposits. The preferred orientations of the deposits were determined by using the following equation (Nayana *et al*., 2011).

$$T_c = \frac{I(hkl)\sum I_o(hkl)}{\sum I(hkl)I_o(hkl)} \times 100 \qquad [1]$$

Where, I (hkl) is the peak intensity of zinc electrodeposit and $\sum$I is the sum of intensities of independent peaks. The index '0' refers to the intensities for standard zinc sample (JCPDS 00-004-0831). The orientation with maximum texture coefficient value is the preferred orientation of the deposit (Berube and Esperance, 1989).

The percentage reflection of deposits was determined using Ocean optics USB 4000 Spectrophotometer, referenced against a silver mirror. The reflectivity of silver mirror was set at 100% and measurements were carried out at different surface points of the deposited sample.

RESULTS AND DISCUSSION

Electrodeposition process

The Hull cell was used to optimize the bath composition containing zinc sulphate, sodium sulphate, CTAB and Boric acid. The CTAB was used as a wetting agent in the electrodeposition process. The concentration of one constituent was varied continuously, while keeping other constituents constant (Nayana *et al*., 2017). The concentration of a particular constituent or operating condition at which good bright deposit is formed over wide current density range was fixed as optimum. The procedure was repeated for all the bath constituents and operating conditions. The optimised bath composition is given in Table 1. The basic bath gave coarse dull deposit between the current density range of $0.2 – 3Adm^{-2}$. The optimized bath in presence of CG gave bright deposit between the current density range of $0.5-5Adm^{-2}$.

Table 1 Optimized bath composition and operating conditions.

Bath constituents	Concentration	Operating conditions
$ZnSO_4.7H_2O$	0.55 M	Anode: zinc plate (99. 9%)
Na_2SO_4	0.26 M	Cathode: mild steel plate
H_3BO_3	0.33 M	pH = 3.2
CTAB	0.01 M	Temperature = 298 K
Brightener(CG)	60 ml/L	Plating time: 10 min
		Current density: 3.5A dm^{-2}

Cyclicvoltammetric studies

Fig.1 shows typical cyclicvoltammograms obtained from the optimized bath in presence and in absence of CG. The voltammetric response gives information regarding the components of deposits and structure of the deposited phases.
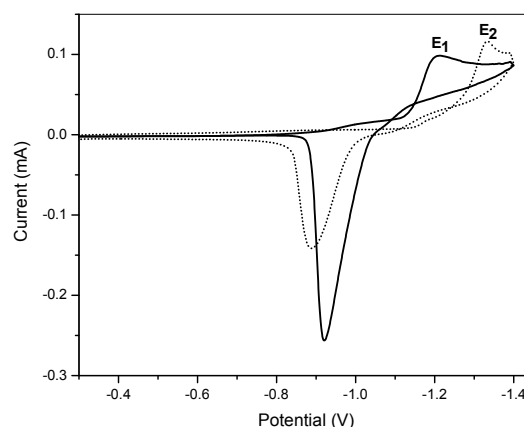
Fig 1 Typical cyclicvoltammograms obtained in presence (solid line) and absence (dotted line) of CG in bath solution.

The voltammogram shows an anodic peak at – 0.9V indicating the oxidation of zinc from η phase of zinc which is almost pure zinc phase (Basavanna S and Arthoba Naik, 2012). The cathodic peak (E_2) at −1.34V observed for the reduction of zinc ions in presence of CG, associated with partial adsorption of CG on the cathodic surface. When CG adsorbs on the cathodic surface it blocks a fraction of active sites ($\theta_{blocked}$) at which the first reduction of zinc process occurs (Ballesteros *et al*., 2007). As a result the reduction of zinc ions occurs only at the fraction of active sites ($1-\theta_{blocked}$) that are not blocked. Hence the current density associated with the reduction of zinc ions decreases with respect to that observed in absence of CG.

When there is an increase in the overpotential then the desorption of CG occurs allowing reduction of zinc ions at active sites. On reversing the sweep direction two current crossovers appear in the cathodic region of voltammogram which indicated three dimensional (3D) nucleation and subsequent crystal growth (Nayana *et al.*,2011). These results indicate that CG is partially adsorbed on the cathode surface and thereby obstructs the dissolution of zinc and enhance the formation of more compact bright deposits.

Chronoamperometric studies

The Chronoamperometric studies were used to identify the zinc nucleation mechanism at different potentials. The primary factor leading to the generation of fine grain deposit is the formation of fresh nucleation sites and their growth rate. This technique has proved to be a powerful means for explaining the mechanism of new phase formation (electrocrystallization process) (Scharifker and Hills,1983). For most of the metals, the charge transfer rate is high and continuous growth of nuclei formed is entirely mass transfer controlled. According to the theory two cases of nucleation can be considered based on the rate of nucleation. In the first case, at increased nucleation rate all nuclei are instantly formed after the potential step and their number remains constant during the growth process. This is called instantaneous nucleation and is given by,

$$I(t) = \left[\frac{zFD^{1/2}c}{(\pi t)^{1/2}} \right] [1 - \exp(-N)] \qquad [2]$$

where I(t) = current density related to the geometric area of the electrode surface, N is the total number of nuclei formed and K is the numerical constant calculated from,

$$K = \left(\frac{8\pi cM}{\rho} \right)^{1/2} \qquad [3]$$

Where M and ρ are the molar mass and metal density, zF is the molar charge of the deposited species, D is the diffusion coefficient, c is the bulk concentration (mol/dm^3).

In the second type, at decreased nucleation rate the nuclei are continuously formed during the entire time, before overlapping of diffusion hemispheres around the growing nuclei is called progressive nucleation [20]. In this type of nucleation the metal clusters of different sizes are formed, especially at the initial time (t). It is described by,

$$I(t) = \left\{ \left[\frac{zFD^{1/2}c}{(\pi t)^{1/2}} \right] \left[1 - \exp\left(\frac{-aN_0Dt^2}{2} \right) \right] \right\} \qquad [4]$$

Where, N_0 is the number density of substrate active sites, 'a' is the steady state nucleation rate constant per site, K' is the numerical constant and is given by

$$K' = \frac{4}{3} \left(\frac{8\pi cM}{\rho} \right)^{1/2} \qquad [5]$$

(Fig.2) shows the potentiostatic current versus time (I–t) transients recorded during the reduction of the zinc in the potential range from −1.20V to −1.24V in absence of CG and −1.22V to −1.34V in presence of CG in the plating bath. The behaviour of these current transients is typical of a nucleation process with 3D growth of nuclei controlled by the diffusion of

the electroactive species. All the curves showed initial sharp rise in short time and the current reaches maximum value (I_{max}). This sharp rise in current is probably due to growth and stabilisation of initial nuclei. The decay in current density after reaching I_{max} of each transient converges almost to a limiting current and nucleation process is controlled by diffusion of zinc ion(Tsay and Hu,2002). The nucleation mechanism is identified by drawing non-dimensional curves and compared with those obtained using the Schariker and Hills model (Scharifker and Hills, 1983) for three dimensional (3D) instantaneous and progressive nucleation process which are under the control of diffusion. The model uses the following equation for finding three dimensional (3D) instantaneous and progressive nucleation processes.
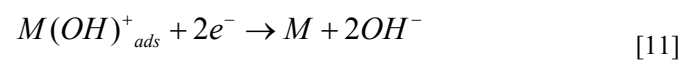
For instantaneous nucleation,

$$(I/I_{max})^2 = \frac{1.2254\left\{1 - \exp\left[-2.3367(t/t_{max})^2\right]\right\}^2}{t/t_{max}} \qquad [6]$$

For Progressive nucleation,

$$(I/I_{max})^2 = \frac{1.9542\left\{1 - \exp\left[-1.2564(t/t_{max})\right]\right\}^2}{t/t_{max}} \qquad [7]$$

Where I is the current density at any instant of time, I_{max} is the maximum current density with respect to maximum time (t_{max}). Hence there are two limiting processes here. Based on equation (6) all nuclei are formed instantly after potential step and is called instantaneous nucleation. Based on equation (7) all nuclei are formed slowly and their number increase during the entire process and hence called progressive nucleation (Basavanna S.and Arthoba Naik, 2011).

Non-dimensional plots obtained with experimental and theoretical data for zinc deposition in absence and presence of CG (Fig.3). (Fig.3A) and (Fig.3B) shows that experimental $(I/I_{max})^2$ curve is much larger than theoretical model after the time maximum(t_{max}). The following mechanism explains the anomalous behaviour of Fe group metal ions on the electrode surface (Tsay and Hu, 2002).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad [8]$$

$$M^{2+} + OH^- \rightarrow M(OH)^+ \qquad [9]$$

$$M(OH)^+ \rightarrow M(OH)^+_{ads} \qquad [10]$$

$$M(OH)^+_{ads} + 2e^- \rightarrow M + 2OH^- \qquad [11]$$

Where M designates Zn, Fe, Co, Ni atoms. The reduction rate of M mainly depends on the stability of $M(OH)^+_{ads}$ or $M(OH)^+$. The nucleation process of zinc deposit is always associated with release of hydrogen which is evident from equation (9). Hence the experimental $(I/I_{max})^2$ should be larger than the theoretical model (Basavana S. and Arthoba Naik, 2009) (Fig.3A) shows the nucleation mechanism of zinc deposition in absence of CG. The rising parts of the transients are located near the instantaneous nucleation curve. As soon as the potential changes to more negative values, the nucleation process does not confirm to either of the models of diffusion-controlled 3D nucleation.
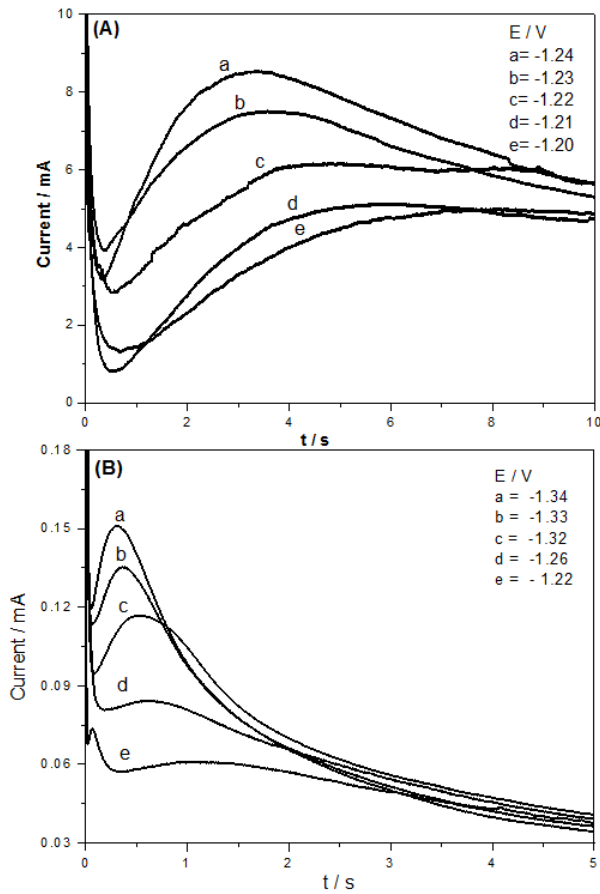
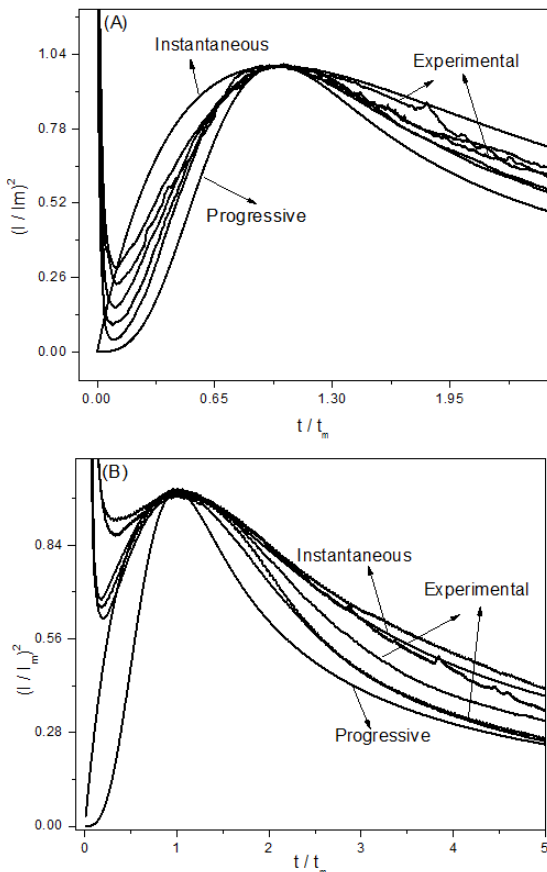**Fig 2** Current transients for zinc electrodeposition A) in absence and B) in presence of CG.
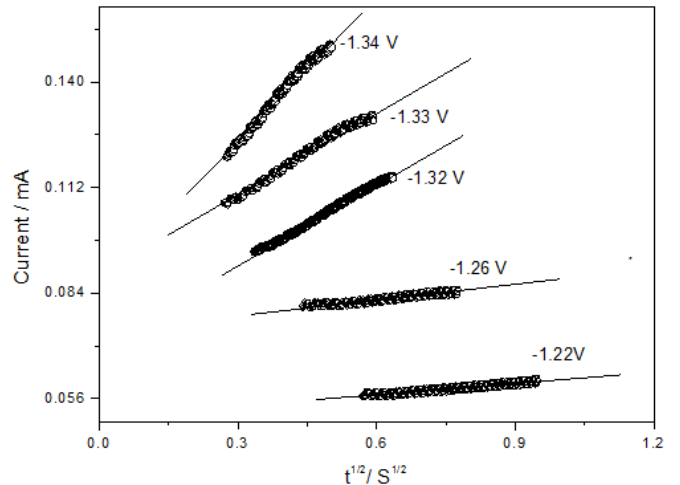

Fig 4 Dependence between I versus $t^{1/2}$ plots for initial transient portion from (Fig.2B)

(Fig.3B) shows the nucleation mechanism of zinc deposition in presence of CG. The rising parts of the transients are located on instantaneous nucleation curve. These results confirmed that the nucleation process occurs by instantaneous nucleation in presence of CG.

Another diagnostic characteristic given by Scharifker and Hills nucleation model is based on the rising part of the current-time transient curves which is based on the early stage deposition analysis (Scharifker and Hills, 1983) It is possible to plot I versus $t^{1/2}$ for instantaneous nucleation and I versus $t^{3/2}$ for progressive nucleation. (Fig. 4) shows the plot of I versus $t^{1/2}$ obtained in presence of CG confirms instantaneous nucleation mechanism under the given experimental conditions.
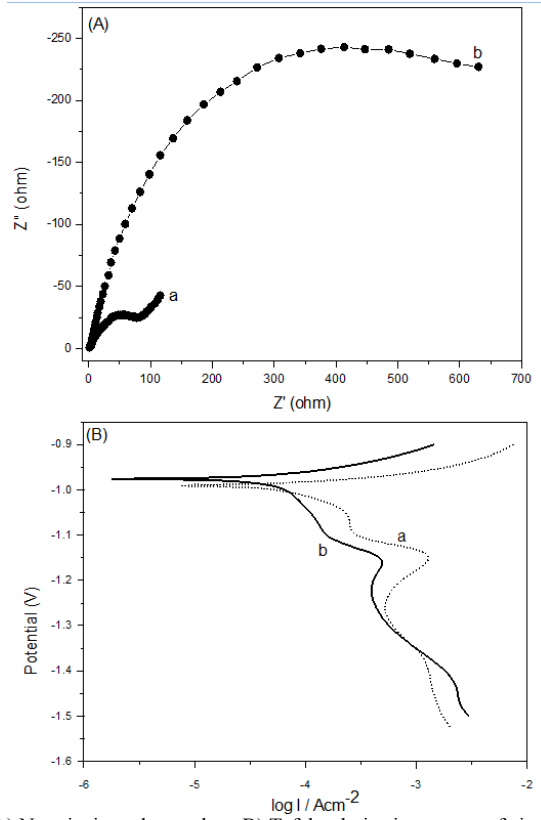
Corrosion resistance studies

Fig 3 Non-dimensional $(I/I_{max})^2$ versus t/t_{max} plot for plating bath (A) in absence and (B) in presence of CG

Fig 5 A) Nyquist impedance plots, B) Tafel polarisation curves of zinc coating in 3.5wt. % NaCl solution. The electrodeposits obtained in absence (a) and in presence (b) of CG.

The corrosion resistance studies were done with Electrochemical Impedance Spectroscopy (EIS) and polarisation technique. (Fig.5A) shows the comparison of Nyquist plots of zinc deposit in absence and presence of CG in the optimized bath. The charge transfer resistance value of the deposit obtained in absence and presence of CG was about 122 and 855 Ω/cm^2 respectively. These results revealed that the bright coating reduces the rate of corrosion of substrate. This is in good agreement with the polarisation results obtained.

The Tafel plots show that the I_{corr} value of bright deposit was 0.04 mA/cm^2 and 0.35 mA/cm^2 for dull deposit (Fig.5B). There is decrease in I_{corr} value and deposition potential (E_{corr}) value shifts in more noble direction indicating the increase in corrosion resistance. These results indicate that the bright deposit can successfully act as a protective layer for mild steel substrate and also improve the corrosion resistance of the bright coating.

SEM analysis and Reflectance studies
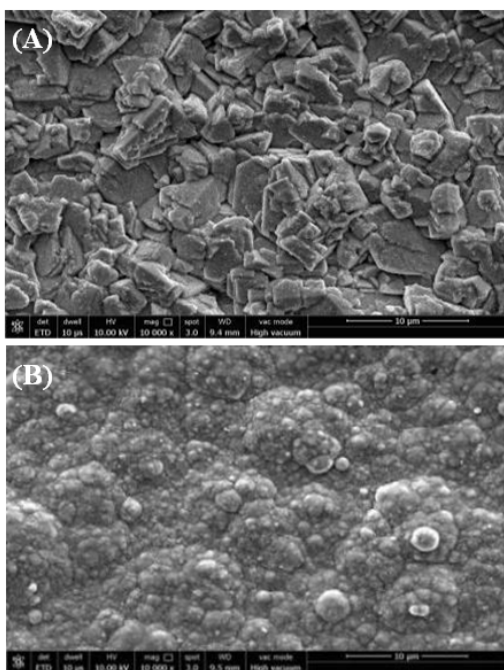
Fig 6 SEM photomicrographs of the deposits obtained in A) absence and B) presence of CG in the plating bath solution.

The SEM image shows non uniform and coarse-grained deposit of zinc obtained in absence of CG (Fig.6A). The addition of CG increases the formation of fresh nucleation sites during deposition and decreases the growth of nuclei, resulting in formation of fine grained deposit (Fig.6B). This leads to the formation of smooth and shiny deposit. The reflectance and degree of total reflection as a function of wavelength of visible light for zinc coating is shown in Fig. 7. It can be seen from the reflectance spectra that the addition of CG into the bath solution leads to an increase in the degree of reflection. Only 3-4% of variation in total reflectance was observed at different surface points of zinc coatings [23]. These results confirmed that CG can be used as a good brightener for zinc coatings.
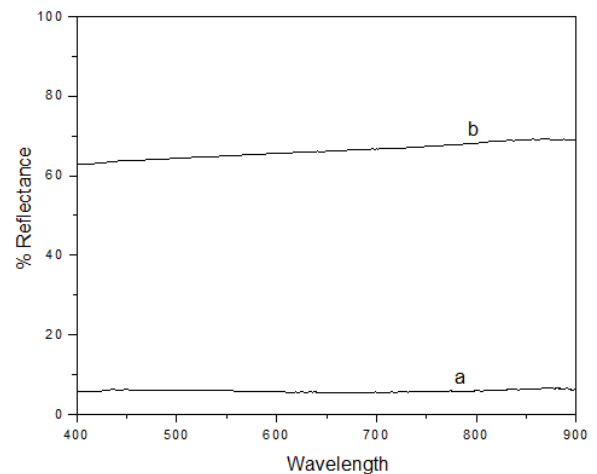

Fig.7 Reflectance spectra of zinc electrodeposition at 3.5A/dm^2 (a) in absence and (b) in presence of CG in the plating bath solution.

XRD Analysis

The XRD pattern for the deposit in basic bath is shown in (Fig.8a) and indicated (102) and (110) as the preferred orientation. This infers that in absence of CG, the zinc crystallites prefer (102) and (110) orientation (Nayana *et al*., 2011). The XRD pattern for the deposit in presence of CG is shown in (Fig.8b) and indicated (110) as the preferred orientation which infers that in presence of CG zinc crystallites prefer (110) orientation. These observed results are in good agreement with the referred data in the literature (Hsieh *et al*., 2008). This preferred orientation arises due to different growth rates of different faces of the crystal which in turn is due to the adsorption of CG on the cathode surface (Reddy, 1963). The morphological and microstructural changes such as refinement in grain structure, smoothening and formation of more predominant preferred orientation along (110) planes of the zinc deposit was responsible for the bright appearance of the coating.

The XRD pattern shows the formation of lines corresponding to η-phase and γ-phase of zinc (Fig.8). All the peaks are corresponding to only zinc metal, indicating that there are no impurities in the deposit. The presence of η-phase content in the bright deposit increases the corrosion resistance of the coating. Hence, these results showed that bright deposit obtained in presence of CG were smooth, compact and fine grained.
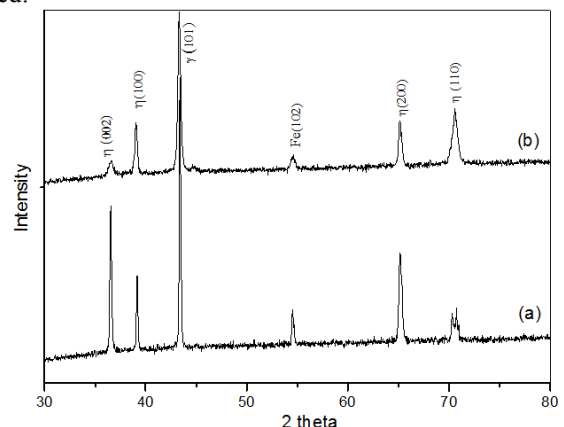
Fig 8 XRD pattern of zinc electrodeposition observed in a) absence and b) presence of CG in the bath solution.

CONCLUSIONS

Bright, zinc coating is obtained in presence of newly synthesized brightener, which is a condensation product of cysteine hydrochloride monohydrate and glutaraldehyde (CG). The chronoamperometric studies revealed that the bright zinc electrodeposition occurs by 3D instantaneous crystal growth mechanism. Corrosion studies confirmed that, presence of brightener in zinc plating bath gives corrosion resistant deposits on mild steel substrates. SEM and reflectance studies confirmed that, presence of CG in the bath solution increases the formation of fresh nucleation sites during deposition, decreases the growth of nuclei and results in the formation of fine grained deposit. The XRD analysis revealed the presence of η-phase in bright deposit, which is responsible for increasing the corrosion resistance of coating. It also showed broadening of peaks in bright deposit which indicates refinement in grain structure of coating. The proposed studies indicate that the newly synthesized brightener can be conveniently used for getting a bright and protective coating to mild steel substrate in large scale applications.

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