

## Electrochemical and reflectance studies of bright Zn-Co alloy coatings

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In the present work, electrodeposition of Zn-Co alloy from sulphate bath has been carried out in presence of brightener, the condensation product of vanillin and serine. The investigation on electrodeposit has been carried out using cyclic voltammetry and galvanostatic techniques, while polarization and electrochemical impedance spectroscopic techniques are used for corrosion studies. It is found that the deposition current density has a great influence on the corrosion resistance nature of the coatings. The reflectance and scanning electron microscopic studies show the formation of bright coatings.

**Keywords:** Brightener, Electrodeposition, Reflectance, Zn-Co alloy

Zinc alloys with eight group metals (Ni, Co and Fe) have attracted a lot of interest as these alloys exhibit significantly higher corrosion resistance than pure zinc and have a potential to replace the toxic cadmium coatings<sup>1-4</sup>. Electrodeposition of these alloys is classified as anomalous by Brenner<sup>5</sup>, because the less noble zinc deposits preferably on the cathode with respect to the more noble one. Several hypotheses have been proposed to explain this anomalous behaviour in terms of precipitation and adsorption of zinc hydroxide film at the electrode surface<sup>6</sup> that induces zinc reduction. This zinc hydroxide film is formed due to the increase in interfacial pH during the simultaneous electrochemical reaction of hydrogen evolution. The Zn-Co alloys obtained by electrodeposition processes, with low percentage of alloying element cobalt (<1%) is the most commercially viable option as it is cost effective and exhibits better corrosion resistance (three- or four-fold) over the existing zinc coating system<sup>7</sup>. Organic additives are often added to the zinc electroplating baths to make the electroplated surface more durable, uniform, and compact for better performances in terms of corrosion protection<sup>8-10</sup>. The concentrations of additives range between 100 mM and 10 mM and prevent whiskers or dendrites formed during the electrodeposition process. The majority of metal electrodeposition process is carried out from baths containing organic additives such as aldehydes, amines and complexing agents<sup>11-15</sup>. These additives are nontoxic, easily available and, upon degradation, the effluent treatment is easier.

The present work emphasizes the influence of brightener [condensation product of vanillin and serine (VS)] on co-deposition of Zn-Co from acid sulphate bath. The electrochemical and corrosion properties of dull and bright Zn-Co alloy deposits are studied.

### Experimental Procedure

The bath solutions were freshly prepared using analytical grade chemicals in double distilled water and used for the experiments without further purification. The standard Hull cell of 267 mL capacity was used to optimize the bath constituents. The Hull cell experiments were carried out without agitation. The pH of the solution was adjusted with 10% H<sub>2</sub>SO<sub>4</sub> 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 plates (AISI-1079) of standard Hull cell size were mechanically 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 then subjected to electrocleaning process. After this the steel plates were washed with water and used for the experiment. After the experiment the plate was removed from the solution and subjected to bright dip in 1% nitric acid for 3–5 s followed by water wash.

The condensation product was prepared from 1:1 stoichiometric amounts of vanillin and serine (vs) in ethanol medium (50 mL), under reflux condition for 3 h at 343 K<sup>16</sup>. The completion of the reaction was confirmed by TLC. The obtained solution was made

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up to 100 mL using double distilled water and the same was used for the experiments. The cyclic voltammetric studies were performed using CHI660D electrochemical workstation. A steel electrode with geometrical area of  $0.07 \text{ cm}^2$ , a platinum wire and saturated calomel were used as working, counter and reference electrodes respectively. Prior to each experiment, the working electrode was polished to a mirror finish with  $0.05 \text{ }\mu\text{m}$  alumina.

The potentiodynamic polarization and electrochemical impedance studies (EIS) were carried out in a typical three electrode system with the coated mild steel electrode (area  $1 \text{ cm}^2$ ) as working electrode. The corrosion behavior of Zn-Co alloy coatings of  $10 \text{ }\mu\text{m}$  thickness, obtained from the optimized bath in presence and absence of VS was studied in 3.5 wt.% NaCl solution. The composition and surface morphology of the deposits on mild steel electrodes ( $2 \times 2 \text{ cm}^2$ ) were examined using an EDX analyser integrated with scanning electron microscope (JEOL-JSM-6400). The Philips X'pert PRO MPD X-ray diffractometer was used to determine the Zn-Co alloy phases present in the deposits. JCPDS powder diffraction file cards were used for phase identification. The percentage reflection of the deposits was determined using Ocean optics USB 4000 spectrophotometer, referenced against a vacuum coated silver mirror. The reflectivity of silver mirror was set at 100% and the measurements were carried out at different surface points of the deposited samples.

## Results and Discussion

### Electrodeposition

Similar to our earlier studies<sup>17-22</sup>, the effects bath constituents, pH, current density, and temperature were optimized by Hull cell experiments. The optimized bath composition was  $0.5 \text{ molL}^{-1}$  zinc sulphate,  $0.05 \text{ molL}^{-1}$  cobalt sulphate,  $0.2 \text{ molL}^{-1}$  sodium sulphate,  $0.02 \text{ molL}^{-1}$  cetyltrimethylammonium bromide (CTAB) and  $0.3 \text{ molL}^{-1}$  boric acid. The CTAB was used as a wetting agent in the deposition process. The electrodeposition was carried out by using optimized bath solution of pH 3.5 at 298K. In the absence of additive, the electrolytic bath gave coarse dull deposit between the current density range of  $1\text{--}3 \text{ Adm}^{-2}$ . In order to improve the nature of the deposit,  $20 \text{ mL L}^{-1}$  of VS was added to the bath solution. The optimized bath solution gave mirror bright deposits between the current density range of  $1\text{--}5 \text{ Adm}^{-2}$ .

### Cyclicvoltammetric studies

The influence of VS on codeposition of Zn-Co alloy was studied using cyclic voltammetric technique. Figure 1 shows typical cyclic voltammograms obtained from the optimized bath solution in presence and absence of additives. The voltammetric response gives information regarding the components of the alloy and structure of the deposited phases. In absence of CTAB and VS in the optimized bath solution, the voltammogram shows one cathodic and two oxidation peaks ( $A_1$  and  $A_2$ ). As suggested by Jovic *et al.*<sup>23</sup> the detection of multiple peaks during the electrochemical oxidation of alloys can be attributed to the dissolution of metals in the alloy via different intermediate phases. The first peak ( $A_1$ ) at potential  $-0.6\text{V}$  corresponds to the oxidation of zinc from  $\alpha$  and  $\beta$ -phases. The second peak ( $A_2$ ) at potential  $-0.4\text{V}$  corresponds to the dissolution of cobalt from  $\alpha$  and  $\beta$ -phases.

The shift in cathodic peak towards more negative direction was observed in presence of VS, associated with the adsorption of VS on the surface of cathode. When the additive adsorbs onto the electrode surface, it blocks a fraction of the active sites ( $\theta_{\text{blocked}}$ ) at which the first reduction process occurs<sup>24</sup>. As a result, the reduction of zinc ions occurs only at the fraction of active sites ( $1 - \theta_{\text{blocked}}$ ) that were not blocked. With an increase in the overpotential and desorption of additive, the reduction of zinc ions at the active sites takes place. When the potential scan is reversed in opposite direction, two anodic peaks with decreasing peak height were observed, corresponding to the dissolution of zinc and cobalt from  $\alpha$  and  $\beta$  phases. These results

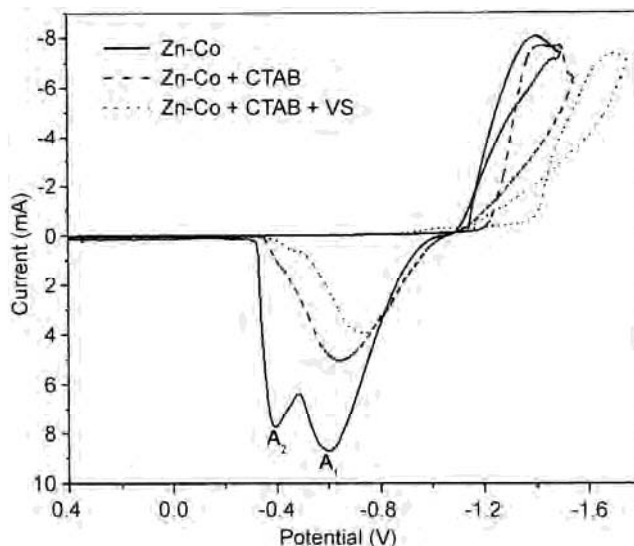


Fig. 1—Typical cyclic voltammograms of Zn-Co alloy in presence and absence of VS in the bath solution

indicate that the VS is partially adsorbed on the steel surface and hence decreases the dissolution process. This confirms the formation of more compact Zn-Co bright deposits in presence of VS in the plating bath.

#### EIS and polarization studies

The electrochemical behavior of Zn-Co deposits was studied using impedance spectroscopy. Figure 2 presents the comparison of Nyquist plots of Zn-Co alloy deposits obtained in absence and presence of VS in the bath solution. Nyquist plots for all the zinc samples exhibit two capacitive semicircles, typical of pure zinc in this corrosive medium<sup>25-27</sup>. To account for the corrosion behaviour of zinc coatings, the simulation program was used to build the proposed equivalent circuit and fit it to the experimental data (inset Fig. 2). The calculated equivalent circuit parameters for zinc deposits with different current densities are presented in Table 1.

The equivalent circuit model suggests the existence of two layers<sup>28</sup>. Kalinauskas *et al.*<sup>27</sup> proposed that the two layers in NaCl solution consist of a compact ZnO and porous  $4\text{Zn}(\text{OH})_2$ ,  $\text{ZnCl}_2$ . With this assumption, the semicircle at high frequencies can be attributed to the presence of  $4\text{Zn}(\text{OH})_2$ ,  $\text{ZnCl}_2$  layer and the semicircle at low frequencies to the compact ZnO layer. The existence of a compact ZnO layer should mean a passivation of zinc deposits in 3.5% NaCl solution. To note that in the absence of VS, the pseudo-capacitance  $Q_2$  is many times greater than  $Q_1$ , whereas the contrary was observed in the presence of VS.

The two charge transfer resistances  $R_1$  and  $R_2$  increase with the increase in the deposition current densities (Table 1) for the optimized bath, which indicate an improvement in the corrosion resistance of the deposits. The fine grain size of the deposits play to improve the corrosion resistance of the deposits obtained in presence of VS. In the absence of VS, the two charge transfer resistances ( $R_1$  and  $R_2$ ) are very weak, compared to those obtained in the presence of VS at a current density of  $5 \text{ Adm}^{-2}$ . This indicates an improvement in the corrosion resistance of Zn-Co deposits obtained in presence of VS and this result is found to be in good agreement with those obtained from potentiodynamic polarization studies. Figure 3 shows Tafel curves for the Zn-Co coatings obtained on the mild steel samples. The corrosion current density ( $I_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) were calculated from the intercept of the Tafel slopes, and are shown in Table 1. It was observed that the values of  $I_{\text{corr}}$  decrease with the increase in the current density. The bright deposits obtained at a current density of  $5 \text{ Adm}^{-2}$  show a least  $I_{\text{corr}}$  value

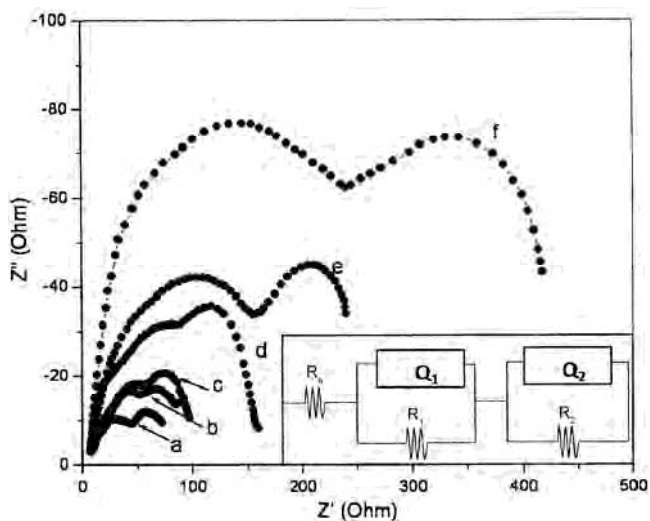


Fig. 2—Nyquist impedance plots of Zn-Co alloy coatings in 3.5 wt% NaCl solution. The electrodeposits obtained at different current densities (a)  $3 \text{ Adm}^{-2}$  in absence of VS, and (b)  $1 \text{ Adm}^{-2}$ , (c)  $2 \text{ Adm}^{-2}$ , (d)  $3 \text{ Adm}^{-2}$ , (e)  $4 \text{ Adm}^{-2}$  and (f)  $5 \text{ Adm}^{-2}$  in presence of VS in the bath solution. Inset shows the equivalent circuit used to fit the Nyquist impedance plots

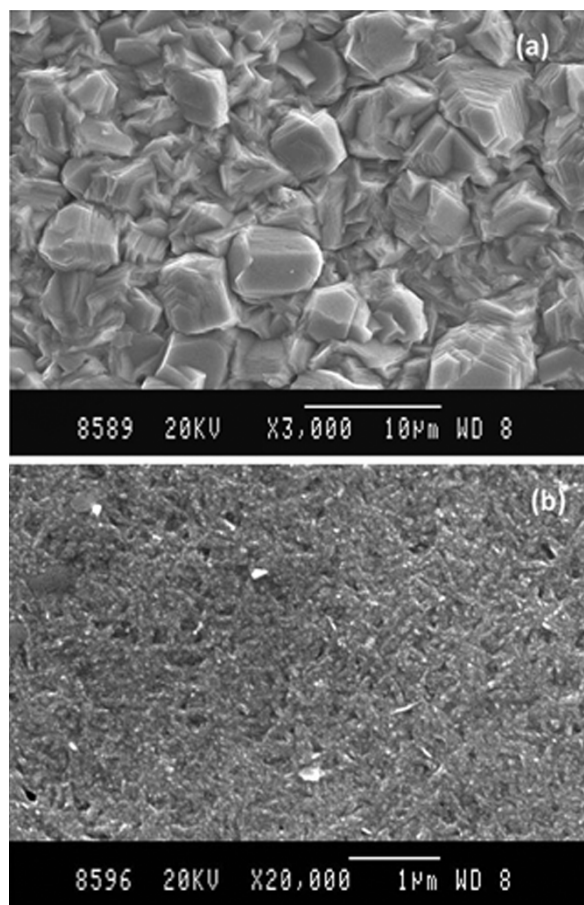


Fig. 3—SEM images of Zn-Co coatings electrodeposited at current density  $4 \text{ Adm}^{-2}$  (a) in absence and (b) in presence of CTAB+VS in the bath solution

Table 1—Parameters for the fitted impedance diagrams and polarization parameters measured for Zn-Co samples in 3.5% NaCl

Current density $\text{Adm}^{-2}$	$R_1$ $\Omega\text{cm}^2$	$R_2$ $\Omega\text{cm}^2$	$Q_1$ $\text{Fcm}^{-2}$	$Q_2$ $\text{Fcm}^{-2}$	$E_{\text{corr}}$ V	$I_{\text{corr}}$ $\text{mAcm}^{-2}$
3 (without VS)	25.4	29.4	14.9	2273	-1.040	2.436
1	47.2	24.7	310.9	12.87	-1.044	1.924
2	54.7	28.8	220.1	9.45	-1.045	1.154
3	93.1	38.9	162.7	7.91	-1.041	1.103
4	116.1	59.7	63.9	3.75	-1.042	0.918
5	211.9	118.1	31.3	3.18	-1.043	0.855

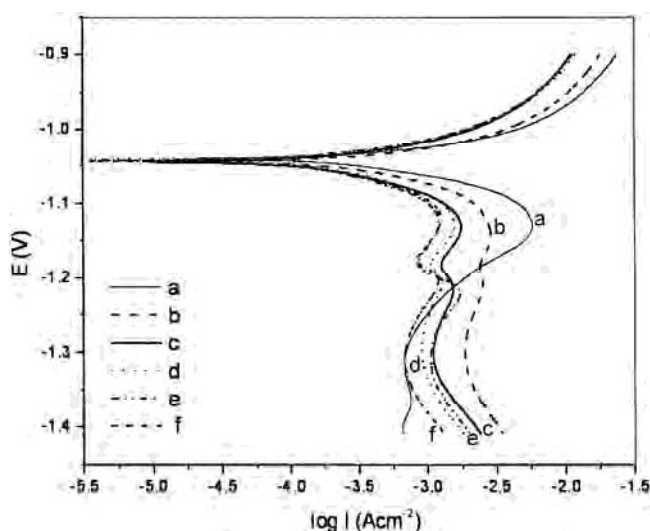


Fig. 4—Polarization curves in 3.5% NaCl for Zn-Co alloys (10  $\mu\text{m}$  thickness) deposited at different current densities [(a) 3  $\text{Adm}^{-2}$  in absence of VS, and (b) 1  $\text{Adm}^{-2}$ , (c) 2  $\text{Adm}^{-2}$ , (d) 3  $\text{Adm}^{-2}$ , (e) 4  $\text{Adm}^{-2}$  and (f) 5  $\text{Adm}^{-2}$ , in presence of VS]

against dull deposit. These results indicate that the bright deposits can act as protective layers and improve the corrosion resistance of mild steel substrates in simulated physiological environment.

#### SEM and reflectance studies

Figure 4 shows the SEM photomicrographs of the deposits obtained in absence and presence of CTAB and VS in the bath solution. Figure 4 (a) shows coarse-grained deposit with non-uniform sized crystals obtained in absence of CTAB and VS. The fine grained and uniform arrangement of crystals, yielding the compact bright coatings were observed in presence of CTAB and VS [Figure 4(b)]. The EDX analysis shows that the percentage of Co in the deposits obtained in absence and presence of VS in the bath solution is 1.2 and 1.5 respectively.

The ideal reflectance and the degree of total reflection as a function of wavelength of visible light

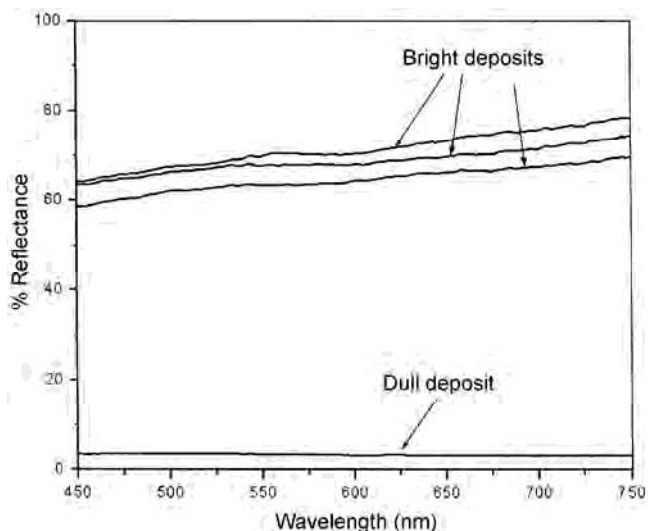


Fig. 5—Reflectance spectra for dull and bright deposits of Zn-Co alloy

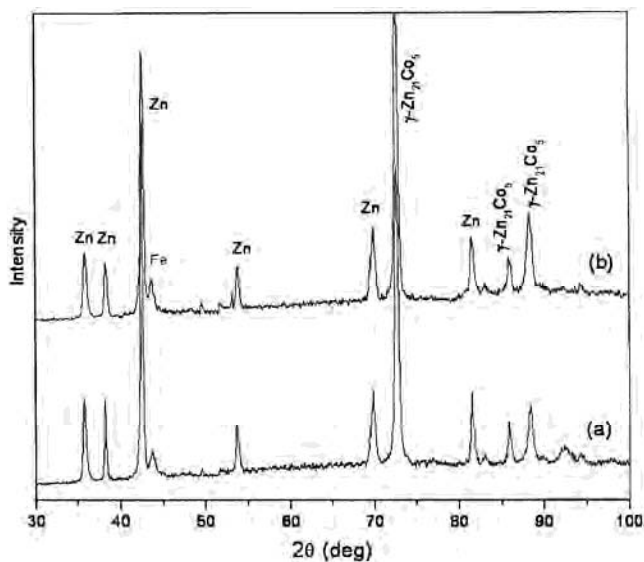


Fig. 6—X-ray diffraction patterns of electrodeposits of Zn-Co alloy (a) in absence and (b) presence of VS

for Zn-Co alloy electrodeposits have been obtained in presence and absence of VS. From Fig. 5 it can be seen that the addition of VS into the bath solution leads to an increase in the degree of reflectance of the deposit. Only 8-10% of variation in the total reflectance is observed at different surface points of Zn-Co alloy coatings. These results confirm that VS acts as a good brightener for Zn-Co alloy deposition.

#### X-ray diffraction analysis (XRD)

The preferential crystal orientation of zinc electrodeposits depends on the experimental conditions<sup>29,30</sup>, such as current density, pH and temperature. The XRD pattern shows (Fig. 6) the

formation of lines corresponding to  $\alpha$ -zinc phase and  $\beta$ - $\text{Co}_5\text{Zn}_{21}$  phase. The broad lines observed in presence of VS confirm the decrease in the grain size of the deposits. The decrease in the grain size is attributed to the adsorption of VS onto the surface of the substrate and hence to the decrease in the co-deposition rate.

### Conclusion

The protective Zn-Co alloy coating was obtained from the acid sulphate bath. The VS increases the corrosion resistance nature of the deposit by decreasing the grain size of the deposit. XRD studies show the presence of  $\alpha$  and  $\beta$ -phases in the deposits. SEM and reflectance studies reveal the formation of fine-grained and bright deposits in presence of VS. The proposed studies indicate that the VS can be used as a brightener for codeposition of Zn-Co alloy in large scale applications.

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