Optimization of Bright Zn-Co-Ni Alloy Coatings and its Characterization

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Abstract- Acidic sulphate bath having ZnSO\textsubscript{4}.7H\textsubscript{2}O, CoSO\textsubscript{4}.7H\textsubscript{2}O, NiSO\textsubscript{4}.7H\textsubscript{2}O and thiamine hydrochloride (THC) and citric acid (CA) in combination, was optimized for deposition of bright Zn-Co-Ni alloy coating on mild steel. Bath constituents and operating parameters were optimized by Hull cell method, for highest performance of the coating against corrosion. The effect of current density (c.d.), on deposit characters, such as corrosion resistance and hardness, thickness were studied and discussed. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods were used to assess the corrosion behaviors. The composition of deposits were determined by spectrophotometric method and confirmed by EDX analysis. Surface morphology of the deposits was examined using scanning electron microscopy (SEM). The Zn-Co-Ni alloy, with intense peaks corresponding to Zn (100) and Zn (101) and Zn (110) phases, showed highest corrosion resistance, evidenced by X-ray diffraction (XRD) study. A new and cheap sulphate bath, for bright Zn-Co-Ni alloy coating on mild steel has been proposed, and results are discussed.

Keywords- Electrodeposition, Phase structure, Surface Morphology, Corrosion Resistance, Ternary Zn–Co–Ni alloy
1. INTRODUCTION

Many efforts have been made to develop bright corrosion resistant steel plates especially for automotive body panels. Recently, it has been shown that electrodeposited zinc-iron group metal alloys are suitable materials for this application [1]. Zinc–nickel alloy coatings are being extensively studied instead of cadmium coating due to their good corrosion protection property [2], better form ability, and improved welding characteristics [3,4]. Zn–Ni alloys containing 15–20 wt.% nickel were shown to possess four times more corrosion resistance than cadmium–titanium deposit [5]. The Zn–Fe alloy is widely used in electroplating procedures due to its low cost. It is well known that Zn–Ni and Zn–Fe alloys are good substitute for cadmium, which has two environmental hazards (cadmium and cyanide). It was observed that the addition of Fe to Zn–Ni alloy has led to the formations of ternary Zn–Ni–Fe alloys, which improve the appearance of the alloy and increase its corrosion resistance [6].

Zn–Ni–Fe alloys are valuable for their leveling action [7] and are used also as a source in hydrogen evolution reaction [8]. Experimental studies have revealed that ternary Zn-M alloys show better electrochemical properties compared to corresponding binary alloys [9]. Further, the ternary Zn-Co-Ni alloys are characterized by enhanced corrosion resistance compared to both binary Zn-Ni and Zn-Co alloys [10]. The increased corrosion resistance of ternary Zn-M alloys compared to Zn-M alloys is due to significantly increased wt.% noble metals in the deposit. The use of specific bath additives was also been found beneficial with respect to corrosion resistance even for low contents of M in the deposit. It has been observed that the ternary alloy Zn-Co-Ni is characterized by enhanced corrosion resistance compared to both binary Zn-Ni and Zn-Co alloys.

Zn-Ni-Fe alloy coatings were found to have better surface appearance than Zn-Ni alloy coatings even without adding any brighteners. The micro hardness of the thin films was found to increase with increasing iron content in the deposit [11]. Abou Krisha et al. [12] have studied extensively the electrodeposition of ternary Zn-Ni-Fe alloy and compared the results with that of Zn, Ni, Fe and Zn-Ni deposition. They showed that increase in corrosion resistance of ternary deposits is not only attributed to the formation of $\gamma$-Ni$_2$Zn$_{11}$ phase but also due to the co-deposition of Fe.

Hoen-Velterop et al. [13] have studied the corrosion properties of electrodeposited Zn-Co-Fe alloys having up to 40 wt.% Co and 1 wt.% Fe on steel using various electrochemical techniques and compared with Zn and Cd coatings in 3.5% NaCl solution. It was found that with an increase in Co content in the coating the open circuit potential (OCP) became more positive than that of the zinc coating. For Co contents higher than 30 wt.%, the OCP shifted close to that of Cd, but still remained electronegative to the steel substrate. The Zn-Co-Fe coatings with $\geq$30 wt.% Co and 1 wt.% Fe are nano-crystalline in nature and show superior corrosion resistance as compared to the Zn, low Co content Zn-Co-Fe and Cd coatings. During longer immersion, Zn-Co-Fe alloys with 34-40 wt.% Co became nobler to steel due to
dezincification of the surface, and correspondingly corrosion c.d. decreased. The corrosion resistances of Zn-Co-Fe alloys determined by the electrochemical techniques are confirmed by salt spray tests.

Thus many research works have been reported on deposition mechanism of Zn-Fe group metal alloys, concentrating on anomalous codeposition; and dependency of deposit characters, with bath constitutions and operating parameters. But no work is reported in relation to optimization and characterization of Zn-Co-Ni alloy bath, using Thiamine hydrochloride (THC) and citric acid (CA) used as a brightener for bright Zn-Co-Ni alloy coatings. In the present study, the role of THC and CA in combination, on electrodeposition of Zn–Co-Ni alloy and its corrosion protection performance are investigated. The focus of this work is to optimize the bath compositions and operating parameters, and characterize the coatings. Techniques such as scanning electron microscopy (SEM), Energy Dispersive X-ray Analysis (EDXA) and X-ray diffraction (XRD) methods were used to characterize the coatings.

2. EXPERIMENTAL

Plating solutions were prepared from reagent grade chemicals and distilled water. Standard Hull cell, of 267 mL capacity was used to optimize bath constituents. All depositions were carried out at 303 K and pH=3.0, except during their variation. Polished mild steel panels were used as cathode (area 7.5 cm²) and pure zinc plate, with same exposed surface area was used as anode. A PVC cell, of 250 cm³ in capacity was used with cathode-anode space of ~5 cm. All depositions were carried out galvanostatically under common conditions of temperature and pH for duration of 10 minutes (for comparison purpose), using sensitive power source (N6705A, Agilent Technologies). Thiamine hydrochloride (THC) and citric acid (CA) in combination, represented as (THC+CA) was used as additive for improving the brightness and homogeneity of the deposit. The constituents and deposition parameters were optimized, based on the appearance and corrosion resistance of the coatings.

In order to evaluate the electrochemical properties of the coatings, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed. All electrochemical tests were carried out using Potentiostat/Galvanostat (VersaSTAT-3, Princeton Applied Research) using a three-electrode cell. The working electrode was coated metal specimen. The counter electrode was a platinum electrode, with same surface area as working electrode. All electrochemical potentials referred in this work are indicated relative to saturated silver/silver chloride electrode (Ag/AgCl/Cl⁻ sat.). The 5% NaCl solution was used as corrosion medium throughout the study. Potentiodynamic polarization study was carried out in a potential ramp of -0.25V to +0.25V around open circuit potential (OCP), at scan rate of 1mVs⁻¹. Corrosion rates were determined by Tafel’s extrapolation method. The impedance measurements were carried out over a frequency range
of 100 kHz to 20 mHz, using sine waves of 10 mV amplitude. Role of additives was investigated by studying the cyclic polarization in a potential range of -1.4V to 0.5V.

The microstructure of the deposits was examined using SEM (JSM-6380 LA from JEOL, Japan). X-ray diffraction (XRD) patterns were collected on a JDX-8P JEOL, Japan, with Cu Kα radiation (k=1.5418 Å) as the X-ray source. While the thickness of the deposits was calculated from Faradays law, it was verified using Digital Thickness Tester (Coatmeasure M&C, ISO-17025). The wt. %Co and Ni in the deposit was estimated by colorimetric method [12]. The hardness of the deposits (~20µm thickness) was measured by Vickers method, using Micro Hardness Tester (CLEMEX). The cathode current efficiency (CCE) of the deposition was determined by knowing the mass and composition of the deposit [14].

3. RESULTS AND DISCUSSIONS

3.1. Hull cell study

The bath composition and operating parameters of Zn-Co-Ni bath have been optimized by conventional Hull cell method [15] at 1.0 A cell current, and temperature 30°C. Varieties of deposits having grayish white/bright/mirror bright/porous black appearance were obtained over the wide range of current density of 1.0-5.0 A dm⁻². Effect of each bath constituents on Hull cell panels were examined in terms of their appearance and surface morphology. The composition and operating parameters of optimal bath is given in Table 1.

Table 1. Both composition and operating parameter of optimal bath for electrodeposition of bright Zn-Co-Ni alloy on mild steel(MS) at 303K

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Amount (g L⁻¹)</th>
<th>Operating parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulphate (ZnSO₄.7H₂O)</td>
<td>50</td>
<td>pH :3.0</td>
</tr>
<tr>
<td>Cobalt sulphate (CoSO₄. 7H₂O)</td>
<td>25</td>
<td>Temperature :303K</td>
</tr>
<tr>
<td>Nickel sulphate (NiSO₄.7H₂O)</td>
<td>100</td>
<td>Anode : Pure zinc</td>
</tr>
<tr>
<td>Citric acid (C₆H₈O₇. H₂O)</td>
<td>4</td>
<td>Current density :3.0A dm⁻²</td>
</tr>
<tr>
<td>Sodium acetate (CH₃COONa.3H₂O)</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Thiamine hydrochloride (C₁₂H₁₇N₂O₂Cl. HCl)</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>
3.2. Effect of current density

3.2.1. Wt.% metal in the deposit

The effect of c.d. on wt.% Co and wt.% Ni were studied using optimized bath. It was found that c.d. plays an important role on both appearance and corrosion performance of the deposit. Increase in the wt.% Co and Ni with increase in current densities was found. The bath follows anomalous codeposition over 1.0 to 5.0 A dm$^{-2}$. The bath produced semi bright deposit at low c.d. side; and a porous bright at high c.d. side. The variation in wt.% of M with c.d. is shown in Table 8.1.2.

3.2.2. Thickness of deposit

The applied c.d. was found to show direct dependency on the thickness of deposit as shown in Table 2. The observed linear dependency of deposit thickness with applied c.d. may be due to the adsorbed metal hydroxide at the cathode, caused by the steady increase of pH due to cathodic evolution of hydrogen gas.

3.2.3. Hardness of deposit

Hardness of the deposit was found to increase with c.d. to a peak value and then decreased as shown in Table 2. But at high c.d., the coating was found to be very thick and hard. However, at very high c.d., the deposit was thick and flaky due to formation of metal hydroxide caused by excessive evolution of hydrogen during plating.

3.2.4. Cathode current efficiency and partial c.d.

Zn-Co-Ni bath produced semi-bright deposits at low c.d. and porous bright deposits at high c.d. A sound deposit of Zn-Co-Ni alloy containing 2.9 wt. % Ni and 0.80 wt.% of Co was obtained at $i= 3.0$ A/dm$^2$. The partial deposition current densities were calculated from the mass gained and the chemical composition of the deposit, using the equation:

$$i = \frac{w c_i n_i F}{A t M_i}$$

Where $i$ is the partial current density of element $I$ (A/cm$^2$), $w$ is the weight of the deposit, $A$ is the surface area of the cathode (cm$^2$), $t$ is the time of deposition, $C_i$ is the weight fraction of the element in the alloy deposit, $n_i$ is the number of electrons transferred per atom of each metal, $F$ is the Faraday’s constant, $M_i$ is the atomic mass of that element. Fig. 1 shows the dependence of the partial current densities, $i_p$ of Zn, Ni and Co on the applied c.d. It is evident that in all cases, the $i_p$ increased as the applied c.d. was increased. Further, it was found that the partial c.d. of Zn is always higher than that of the Ni and Co, forming the anomalous co-deposition. Dividing the sum of the partial current densities of Zn, Ni and Co by the applied c.d. resulted in values essentially identical to those of the CCE.
3.3. Corrosion study

3.3.1. Potentiodynamic polarization study

The corrosion behaviors of Zn-Co-Ni coatings were evaluated by electrochemical methods and their corrosion potential ($E_{\text{corr}}$), corrosion c.d. ($i_{\text{corr}}$) and corrosion rate (CR) are reported in Table 2. The CR was found to decrease with c.d. and reached minimum (at optimal c.d.) and then increased. The polarization behaviors of Zn-Co-Ni at different c.d. are shown in Fig. 2. It may be observed that at optimal c.d., i.e. at 3.0 A dm$^{-2}$, the coating having 2.9 wt.% Ni and 0.80 wt.% Co displayed least CR (=0.39×10$^{-2}$ mm y$^{-1}$). In case of the ternary alloy, the corrosion potential was most sensitive to the c.d. at which the coating was deposited. From the Table 2 it is evident that the less CR’s are related neither to high content of the nobler metal, nor to the thickness of coating. The coating at very high c.d. was found to show lower corrosion resistance, due to higher level of porosity.
Table 2. Corrosion parameters of Zn-Co-Ni alloy coatings, deposited from optimized bath at different c.d.’s at 303 K

<table>
<thead>
<tr>
<th>c.d. (A dm(^{-2}))</th>
<th>Wt.% Ni</th>
<th>Wt.% Co</th>
<th>CCE (%)</th>
<th>VHN</th>
<th>Thickness (µm)</th>
<th>(-E_{\text{corr}}) V vs. Ag/AgCl/Cl(_{\text{sat}}) (µA cm(^{-2}))</th>
<th>(i_{\text{corr}}) (µA cm(^{-2}))</th>
<th>CR×10(^{2}) (mm y(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>4.3</td>
<td>0.43</td>
<td>95.1</td>
<td>139</td>
<td>7.8</td>
<td>1.240</td>
<td>1.922</td>
<td>2.82</td>
</tr>
<tr>
<td>2.0</td>
<td>2.2</td>
<td>0.61</td>
<td>97.7</td>
<td>158</td>
<td>12.3</td>
<td>1.212</td>
<td>1.912</td>
<td>2.78</td>
</tr>
<tr>
<td>3.0</td>
<td>2.9</td>
<td>0.80</td>
<td>98.0</td>
<td>189</td>
<td>17.5</td>
<td>1.313</td>
<td>0.274</td>
<td>0.39</td>
</tr>
<tr>
<td>4.0</td>
<td>3.8</td>
<td>1.10</td>
<td>97.5</td>
<td>206</td>
<td>22.7</td>
<td>1.290</td>
<td>1.212</td>
<td>1.76</td>
</tr>
<tr>
<td>5.0</td>
<td>7.4</td>
<td>1.20</td>
<td>95.3</td>
<td>198</td>
<td>24.6</td>
<td>1.254</td>
<td>1.861</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Fig. 2. Potentiodynamic polarization curves of Zn-Co-Ni alloy coatings developed from optimized bath at different current densities
3.3.2. Electrochemical impedance spectroscopy

In EIS, the response of an electrode to alternating potential signals of varying frequency is interpreted on the basis of circuit models of the electrode/electrolyte interface through Nyquist plots. The EIS Nyquist plots of Zn-Co-Ni coatings developed at different c.d.’s are shown in Fig. 3. The significantly higher impedance and larger diameter of (unfinished) semicircle in the case of the ternary alloy at optimal c.d. evidences its high corrosion resistance. The capacitive impedance at high frequencies is well related to the thickness and the dielectric constant of the film.

![Nyquist spectra of Zn-Co-Ni alloy coatings deposited from the optimized bath at different applied current densities (frequency range of 100 kHz to 20 mHz, using sine waves of 10 mV amplitude)](image)

**Fig. 3.** Nyquist spectra of Zn-Co-Ni alloy coatings deposited from the optimized bath at different applied current densities (frequency range of 100 kHz to 20 mHz, using sine waves of 10 mV amplitude)

Fig. 3 can be simulated to the equivalent circuit. Based on the experimental observations, a common electrical equivalent circuit composed of inductive/capacitive/resistive elements in series and parallel, with circuit description code LR(C(R)(Q(R(LR)(CR)))) was proposed. Experimental and simulated data fitment was made using built-in software (ZsimpWin 3.21). It is seen that there is a good agreement between the experimental and simulated data. A best agreement was obtained when a constant phase element was used instead of a pure capacitance, as shown in Fig. 4.
### 3.3.3. Cyclic polarization study

The corrosion process of Zn-Co-Ni alloy can be better understood by studying its cyclic polarization behavior is shown in Fig. 5. The arrow marks indicate the direction of potential scanning. The potential is swept in a single cycle and the size of the hysteresis is examined along with the differences between the values of the starting and ending OCP. The existence of the hysteresis is indicative of pitting, while the size of the loop is related to the amount of pitting taken place during corrosion.

**Fig. 4.** Equivalent circuit model proposed for impedance spectrum of Zn-Co-Ni alloy coating deposited at 3.0 A dm\(^{-2}\)

**Fig. 5.** Cyclic polarization behavior of Zn-Co-Ni coating developed from the optimized bath at i=3.0 A dm\(^{-2}\) and potential range of -1.4 V to 0.5 V
3.4. XRD study

The phase studies of electrodeposited Zn-Co-Ni alloys, having different compositions were characterized by means of X-ray diffraction study. X-ray diffraction pattern of Zn-Co-Ni alloy coatings at different deposition c.d.’s is shown in Fig. 6. It may be observed that the intensity of the peak corresponding Zn(110) increases progressively with c.d. (from 3.0-5.0 A dm$^{-2}$). The Zn(110) reflection was the strongest of zinc, indicating preferred orientation of this phase. This change in phase structure has been observed with different appearance in SEM images.

![XRD patterns of Zn-Co-Ni coatings developed at different c.d. from the optimized bath, showing the change of phase structure with c.d.](image)

**Fig. 6.** XRD patterns of Zn-Co-Ni coatings developed at different c.d. from the optimized bath, showing the change of phase structure with c.d.

3.5. Surface study

The changes in the surface structure of the deposits can be observed from the SEM analysis. Fig. 7 shows the surface topography of Zn-Co-Ni electrodeposits at different c.d.’s. It was observed that at low c.d., the deposit is thin, non-uniform and porous with dull appearance, as shown in Fig. 7(a). Relatively smooth, uniform and bright deposit was obtained at optimal c.d. (3.0 A dm$^{-2}$), as shown in Fig. 7(b). But at higher c.d. porous deposit was found in Fig. 7 (c). The EDX spectra of Zn-Co-Ni alloy deposit at $i=3.0$ A dm$^{-2}$ is shown in Fig. 8. The wt. % Co and Ni was found to be comparable with that determined by colorimetric method.
Fig. 7. SEM micrographs of monolayer Zn-Co-Ni coatings developed from the optimized bath at different current densities: (a) 2.0 A dm$^{-2}$, (b) 3.0 A dm$^{-2}$, (c) 4.0 A dm$^{-2}$
4. CONCLUSIONS

A sulphate bath for deposition of bright Zn-Co-Ni bath has been proposed for better corrosion resistance of MS using THC and CA as additives. Based on the experimental results, it was concluded that:

1. In each c.d., the concentrations of Ni and Co in the ternary alloy coatings were found to be slightly higher than in their binary alloy coating. Hence, nickel and cobalt had a synergistic catalytic effect for deposition.

2. A small increase in the noble metal content in binary alloy bath led to substantial decrease in the CR of the coatings.

3. Zn-Co-Ni alloy coating at $i = 3.0 \text{ A dm}^{-2}$ with 2.9 % Ni and 0.80 % Co showed least CR ($0.39 \times 10^{-2} \text{ mm y}^{-1}$) which is about 18 times less compared to binary Zn-Ni ($7.34 \times 10^{-2} \text{ mm y}^{-1}$ at $i = 3.0 \text{ A dm}^{-2}$) and Zn-Co ($7.08 \times 10^{-2} \text{ mm y}^{-1}$ at $i = 4.0 \text{ A dm}^{-2}$) alloys.

4. XRD study shows that the Zn(110) is the prominent phase, which may be responsible for peak corrosion resistances of ternary alloy coating. Large decrease in corrosion rate of ternary alloy is due to significant change in the crystal lattice of the coatings.

5. The SEM images of electrodeposits confirmed that superior corrosion resistance of Zn-Co-Ni alloy due to improved homogeneity of the coatings.

REFERENCES
