Development of Zn–Ni–Cd coatings by pulse electrodeposition process

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Abstract

A pulse electrodeposition process was developed for the synthesis of Zn–Ni–Cd alloys with cadmium contents between 2 and 7 wt.%. The alloy was deposited from an alkaline bath (pH=9.3). The results indicated that the average current density and pulse current on time (T_{on}) control the corrosion potential and the composition of the resultant alloys. An increase in average current density resulted in a decrease in both nickel and cadmium content in the alloy. At lower T_{on} time (0.5 ms), higher percentages of zinc and cadmium were deposited. The barrier properties of Zn–Ni–Cd alloys plated using different average current densities were evaluated by using mechanical, electrochemical and ASTM B117 salt spray tests and compared with commercial Zn–Ni and Cd deposits. The results indicated that Zn–Ni–Cd alloys exhibit superior barrier properties when compared to Cd or Zn–Ni coatings.

Keywords: Ternary alloys; Pulse deposition; Cadmium alternate; Cadmium depletion; Corrosion rate and microhardness

1. Introduction

Cadmium has been the choice of corrosion resistant coating in aerospace, electrical, and fastener industries due to its excellent corrosion resistance and engineering attributes [1]. Generally, cadmium plating is done using cyanide baths, which are subject to stringent regulations [2]. Alternate baths for cadmium plating are also undesirable because of the toxicity of the metal and its salts [3]. Another drawback is the introduction of large amounts of hydrogen into the underlying metal during deposition process which increases the risk of failure in the structure due to hydrogen embrittlement [4]. Environmental safety and performance needs forced the researchers to look for alternative coatings to the existing cadmium coatings [5].

Zinc–nickel alloy coatings have been suggested in the literature as replacement for cadmium coating because this alloy provides good corrosion protection on steel [6–8] superior formability, and improved welding characteristics [9–11]. Zn–Ni alloys containing 15–20 wt.% nickel have been shown to possess four times more corrosion resistance than cadmium–titanium deposit [12]. However, due to the high zinc content in the deposit, these alloys have more negative potential than cadmium and hence dissolve rapidly in corrosive environments. Although Ni is more noble than Zn, the co-deposition of Zn–Ni is anomalous and a higher percentage of Zn is present in the final deposit. The mechanism for this preferential deposition has been discussed extensively in the literature [13,14].

Typical nickel composition in the alloy is approximately 5–10%, and any further increase in nickel composition is based on using a higher-than-predicted Ni/Zn ratio in the bath [15–17]. An enhancement in the nickel composition would lead to more positive open-circuit potential, which in turn will reduce the driving force for the galvanic corrosion. The barrier properties associated with nickel-rich deposits are also superior compared to other coatings [18–20]. Zn–Ni alloys prepared by the pulse process [21] and a multilayer approach [22] were also adopted in order to obtain high corrosion resistant alloys. Zn–Sn alloys have also been synthesized and their corrosion behavior was evaluated [23, 24]. Several attempts have been made to decrease the anomaly and increase the nickel content either by introducing inert species in the bath or by developing a ternary alloy [25–29]. Co-deposition of phosphorous along with Zn–Ni improves the corrosion [25] and hydrogen permeation [26] characteristics of the electrodeposits. Zn–Ni–P alloys possess better corrosion properties and inhibit the hydrogen entry in the substrate when compared to Zn–Ni alloy [26–28]. Use of Zn–Mn alloys have also been explored by different researchers for corrosion protection [29–31].

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Zhou and Keefe [32] studied the effect of tin addition on the anomalous deposition of Zn–Ni alloy. The nickel ratio increased from 6 to 8% with the addition of small amounts of tin. However, the observed small increase of Ni content in the alloy did not improve the Zn–Ni barrier properties. Zn–Ni–Cd alloys have also been synthesized in our laboratory using both acid and alkaline baths by DC deposition [33,34].

The objective of this work was to develop a pulse electrodeposition process for plating of Zn–Ni–Cd ternary alloys, which will induce barrier properties to the sacrificial Zn–Ni alloy thereby extending the life of the coating. By introducing the third element (Cd) in the Zn–Ni alloy, the Zn content in the alloy is expected to decrease and consequently decreases the Zn–Ni alloy corrosion potential from −1.14 V vs. SCE to the potential close to cadmium coatings.

2. Experimental

2.1. Sample preparation

Plating and subsequent corrosion studies were done on low-carbon cold-rolled steel plates of 0.8 mm thick and 5.0 × 2.5 cm in area. Initially, the steel samples were mechanically polished with successively finer grades of emery paper. They were then degreased with soap water and rinsed with de-ionized water. Next, the samples were treated in 10% (v/v) H2SO4 solution for 1 min to remove any adherent oxide layer present on the surface. Finally, the samples were again washed in de-ionized water. This procedure was repeated until a clean and smooth surface was obtained. Samples for ASTM B117 testing were prepared using 6″ × 3″ steel panels purchased from Q-Panels, USA.

2.2. Electrolyte preparation and pulse electrodeposition process

Zn–Ni–Cd alloy deposition was carried using an alkaline bath with a pH of 9.3 at room temperature. The composition of

Table 1
Materials and composition used for pulse Zn–Ni–Cd plating

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO4·6H2O</td>
<td>120</td>
</tr>
<tr>
<td>ZnSO4·7H2O</td>
<td>180</td>
</tr>
<tr>
<td>CdSO4</td>
<td>0.5–3.0</td>
</tr>
<tr>
<td>C6H5Na3O7·2H2O</td>
<td>160</td>
</tr>
<tr>
<td>(NH4)2SO4</td>
<td>60</td>
</tr>
<tr>
<td>Dextrin</td>
<td>0.5–0.9</td>
</tr>
<tr>
<td>NH3OH (28%)</td>
<td>~200 ml</td>
</tr>
<tr>
<td>pH</td>
<td>9.3–9.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>RT</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of current density on Zn, Ni and Cd content (DC deposition).

Fig. 2. SEM picture of Zn–Ni–Cd alloy deposited by DC electrodeposition process (4 mA/cm² average current density, magnification X3000).

Fig. 3. Effect of average current density on (a) Zn and Ni and (b) Cd content.
the bath and plating conditions are presented in Table 1 [34]. Ammonium hydroxide was used to adjust the pH of the bath. The ammonium hydroxide also acts as a complexing agent thus preventing the precipitation of the metal ions as hydroxides during addition. The pH of the bath was maintained at 9.3. The pulse electrodeposition process was done by varying pulse parameters such as, average current density ($i_a$), pulse current “on” time ($T_{on}$) using a pulse generator (Plating Electronic GmbH, Model pe86-20-5-25-S-GD). The effect of cadmium sulfate addition was also studied by changing the same from 0.5 g/l to 3 g/l. The potential during pulse deposition was monitored using an EG and G PAR 173 potentiostat/galvanostat using the substrate, platinum mesh and saturated calomel electrode (SCE) working as, counter and reference electrodes respectively.

2.3. Material characterization and mechanical properties evaluation

Energy Dispersive Analysis using x-rays (EDAX) was used to analyze the distribution of the elements in the final deposit. To ensure accuracy of the element distributions, EDAX was done at several points on the surface of the substrate. The accuracy of the measurements for the equipment used was rated at ±0.1 wt.%. The surface morphology and the microstructure of the coating were analyzed using Scanning Electron Microscopy.
Microscopy by means of ESEM FEI Quanta 200 Scanning Electron microscope coupled with EDAX. X-Ray diffraction was performed (Rigaku D/Max-2200 powder X-Ray Diffractometer) using CuKα radiation.

The mechanical characterization studies such as adhesion and microhardness were performed according to ASTM B571-97 and ASTM B 578-87 respectively. A Vickers hardness indenter (Buehler Micromet 1 Micro hardness Tester) was used to indent the prepared Zn–Ni–Cd alloys containing 3 and 7 wt.% Cd with a diamond tip. Commercial Zn and Zn–Ni deposits were also subjected to hardness measurements for comparison. The physical deformation that occurs during the indentation process at an applied load of 100 g for 10–15 s was observed under a microscope and the dimensions of the depression were marked. Vickers hardness number (VHN) was calculated based on the observations made on the indent using the formula

$$VHN = \frac{2P}{d^2} \sin \left( \frac{\alpha}{2} \right)$$

where, $d$ is the diagonal length left by the diamond shaped pyramid indenter. The angle between the phases of the pyramid is $\alpha = 136^\circ$. $P$ is the load used in kilograms and the units of $d$ are in millimeter.

2.4. Electrochemical characterization and salt spray test

A variety of electrochemical techniques such as linear polarization and Tafel polarization were used to evaluate the barrier resistance properties of the coating. The electrochemical characterization was done using an EG and G PAR model 273A potentiostat/galvanostat interfaced with a computer and a three-electrode setup in 0.5 M sodium sulfate and 0.5 M boric acid (pH=7) solution. The steel substrate with the coating was used as the working electrode and a platinum mesh was used as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials in this study are referenced to the SCE. ASTM B117 salt spray test was performed using Atotech environmental test chamber model P22E001 to evaluate the first grey and red rust formation time.

3. Results and discussions

3.1. Effect of average current density

Prior to the pulse electrodeposition of Zn–Ni–Cd alloys, DC electrodeposition was done to determine the average current density for the pulse deposition and to understand the effect of current density on the composition of the final deposit. As can be seen in Fig. 1, increase in the current density increased the Zn content and saturated at 10 mA/cm². At the same time the cadmium content decreased with increase in the current density due to the increase in the over potential which favors the zinc deposition. No significant change in the nickel content was observed with increase in the current density. Fig. 2 shows the scanning electron micrograph of the Zn–Ni–Cd alloy deposit at a current density of 4 mA/cm². It can be seen that the particles are non-uniform and that the size is 10 to 15 μm.

The effect of average current density on the pulse deposited alloy composition was studied by varying the average current density between 4 and 10 mA/cm², while fixing the duty ratio at 0.1. Fig. 3 (a and b) shows the effect of average current density on the Zn, Ni (Fig. 3a) and Cd (Fig. 3b) weight percentages. It is evident from the figure that increasing the average current density resulted in a decrease in both nickel and cadmium content and an increase in the zinc content. This is because at higher average current densities, the over potential favors the zinc deposition. Nearly 19% Ni was obtained at room temperature along with 6% Cd and 75% Zn in the final deposit. It was noticed that in the case of Ni, the weight % did not change drastically and it varied between 18 and 19.5% for a wide range of average current densities (4 to 10 mA/cm²). Significant change in the respective weight % was observed in the case of Zn (between 74 and 80 wt.%) and Cd (between 2 and 7 wt.%). The current efficiency of the Zn–Ni–Cd deposition process was in the range between 75 and 85% and it decreased at higher current densities due to the competing hydrogen evolution reaction.

Fig. 4 shows the change in thickness of the coating and cadmium weight % with respect to the change in average current density. It can be seen that the increase in average current density resulted in an increase of the coating thickness while the cadmium content in the ternary alloy decreased. Thus, the coating thickness is mainly comprised of larger amount of
zinc with \( \sim 19\% \) Ni and the rest is cadmium. It is presumed that, the cadmium is evenly distributed along the Zn–Ni matrix providing improved mechanical and electrochemical properties which has been discussed in the following sections.

Fig. 5 (a–d) shows the effect of average current density on the surface morphology of Zn–Ni–Cd alloy deposits. It is seen that increase in average current density resulted in increased particle size of the final deposit. At lower current densities (4–6 mA/cm\(^2\)), smaller particles in the range 1–2 \( \mu \)m are observed and at higher current density (10 mA/cm\(^2\)), particles exceeding 3–4 \( \mu \)m are seen. This is due to the preferred homogeneous nickel deposition at lower current densities and that of zinc at higher densities which leads to agglomeration of particles resulting in larger particles.

3.2. Effect of \( T_{on} \) time

Fig. 6 (a and b) show the effect of \( T_{on} \) time on the composition of Zn–Ni–Cd alloys at a constant \( T_{off} \) time of 100 ms and an average current density of 4 mA/cm\(^2\). The \( T_{on} \) time was varied from 0.5 ms to 50 ms. The figure depicts that at lower \( T_{on} \) time higher percentage of zinc was obtained since zinc deposition is mass transfer controlled and there is enough time for the zinc ions to migrate towards the electrode/electrolyte interface. It is also seen from the figure that higher amount of cadmium was deposited at the cost of zinc and no change in nickel content was observed above 0.5 ms \( T_{on} \) time. The change in \( T_{on} \) time also modified the morphology of the final deposit which is seen in Fig. 7 (a–d). At lower \( T_{on} \) time (0.5 ms) the particles are smaller (less than 1 \( \mu \)m) and larger particles (greater than 3 \( \mu \)m) are seen at high \( T_{on} \) time (50 ms). It has been reported in the literature\([35,36]\) that \( T_{on} \) and \( T_{off} \) do not have the same influence on the structure of the final deposit because each system may react differently during the electrocrystallization/nucleation process. In the case of single metal pulse electrodeposition such as zinc\([35]\), gold\([37]\), and palladium\([38]\), a reverse trend, that is a decrease in the grain size with an increase in \( T_{on} \) time has been reported due to the increase in nucleation rate resulting from higher overpotential. Also, when the duty cycle (\( T_{on}/(T_{on}+T_{off}) \)) is approaching direct current electrodeposition, an increase in the grain size has been reported\([38]\). In our study the maximum duty cycle employed

Fig. 7. SEM pictures of Zn–Ni–Cd alloys prepared at different \( T_{on} \) times (a) 0.5 ms, (b) 1 ms, (c) 10 ms and (d) 50 ms. (\( T_{off} \) — 100 ms).
was 33% ($T_{on}=50$ ms and $T_{off}=100$ ms). Since the present study involves ternary alloy deposition, it is very hard to explain the observed increase in the grain size with increasing $T_{on}$ time. Nevertheless, it can be attributed to the higher cadmium content in the final deposit at increased $T_{on}$ time.

### 3.3. Effect of CdSO$_4$ content

The effect of presence of cadmium sulfate (CdSO$_4$) in the bath on the final deposit composition was studied by varying the cadmium sulfate content between 0.5 and 3 g/l at two different average current densities (4 and 6 mA/cm$^2$) and a constant duty cycle (0.1). Fig. 8 (a and b) show that at 4 mA/cm$^2$ increasing the cadmium sulfate in the bath decreases the zinc content and not the nickel content. The zinc content decreased from 77% to 57%, while the CdSO$_4$ was increased from 0.5 to 3 g/l. The figure also shows that the composition can be easily controlled when lower amount of CdSO$_4$ (0.5 and 1 g/l) is introduced in the bath. It was observed that the cadmium percentage was constant up to 2 g/l CdSO$_4$ concentration and non-uniform surface was obtained at 3 g/l due to higher cadmium content (~16 wt. %). It is observed that Cd content is 12 wt.% at 6 mA/cm$^2$ when compared to 16 wt.% at 4 mA/cm$^2$ current density. Also, small change in Ni content (~3 wt.% was observed when an average current density of 4 and 6 mA/cm$^2$ was used for the deposition process.

### 3.4. Cadmium depletion study

The change in cadmium percentage in the final deposit with number of deposition was studied by estimating the cadmium weight percentage of the 1st, 2nd, 4th, 6th, 8th and 10th deposits (Fig. 12). The study was carried out with different amounts of initial cadmium sulfate content (1, 2 and 3 g/l) in the plating bath. It was observed that the cadmium percentage was constant up to 4–5 depositions and afterwards it started to decrease. The cadmium content was approximately 5 wt.% in the final deposit up to 4 depositions when the initial CdSO$_4$ content was 1 g/l. Subsequent depositions resulted in Zn–Cd (85% Zn and 15% Ni) 78.4 and 82.25° [39,40]. Also, there was no inclusion of Cd in to the Zn–Ni alloy with the depletion of cadmium ions in the bath. Higher initial CdSO$_4$ content (2 and 3 g/l) lead to constant cadmium content in the final deposit but the surface morphology was not uniform due to higher amounts of cadmium (14 and 20 wt.% respectively). Further studies are necessary to develop a process with capability to deposit cadmium consistently irrespective of the number of deposition. To fulfill this task, addition of an electrocatalytic mixture comprising cadmium salt and other organic additives at regular interval has been carried out [33].

### 3.5. X-Ray diffraction studies

Fig. 13 shows the X-Ray diffraction patterns of base substrate (steel), Cd, Zn–Ni–Cd (DC), Zn–Ni–Cd (PC, 7 wt. % Cd), Zn–Ni–Cd (PC, 3 wt.% Cd) and Zn–Ni (85% Zn and 15% Ni). Cadmium exists in hexagonal phase ($a=b=2.979$ and $c=5.618$) with distinct peaks at 20 values 31.92, 34.52, 38.44, 47.92, 61.2, 62.36, 71.72 and 75.64°. The Zn–Ni alloy with the composition of 85 wt.% Zn and 15 wt.% Ni exhibits prominent peaks at 20 values 42.6 (γ phase, Ni$_5$Zn$_{21}$), 44.35, 62.05 (γ phase, Ni$_5$Zn$_{21}$) 78.4 and 82.25° [39,40]. The slight shift of the peak at 2θ value 62.05 of Zn–Ni to 62.44 in the case of Zn–Ni–Cd (DC), Zn–Ni–Cd (PC, 7 wt.% Cd), Zn–Ni–Cd (PC, 3 wt.% Cd) can be attributed to the inclusion of Cd in to the Zn–Ni alloy phase. Also, there was no difference observed in the diffraction patterns of Zn–Ni–Cd...
samples suggesting that they exist in similar phase irrespective of the preparation method and/or cadmium content. Therefore, it is difficult to explain the better corrosion protection property of both the pulse plated Zn–Ni–Cd deposits than the DC deposited Zn–Ni–Cd using X-Ray diffraction data. Nevertheless it can be attributed to the uniform distribution of Cd in to the Zn–Ni matrix which has been discussed in the following section.

3.6. Mechanical properties

Table 2 lists the composition of different alloy deposits and their mechanical properties such as adhesion and microhardness. Commercial Zn–Ni and Cd deposits were also tested for comparison. The qualitative test for adhesion showed no peeling and/or flaking in the case of commercial Zn–Ni, Cd and pulse deposited Zn–Ni–Cd alloys at 4X magnification when the deposits were bent 180°. In the case of DC deposited Zn–Ni–Cd alloys, the coating was separated after the test indicating its unsatisfactory adhesion with the steel substrate.

The table also shows the results obtained from Vickers Hardness Test. The hardness number is indicated as VHN$_{100gf}$. The hardness values for pure cadmium, Zn–Ni (with 12% Ni) and DC deposited Zn–Ni–Cd alloys are VHN$_{100gf} = 108.78$, 96.52 and 161.71 respectively. Both the pulse deposited Zn–Ni–Cd alloys showed higher hardness values (VHN$_{100gf} = 205.62$ and 215.18 for 3 and 7% Cd respectively) than other coatings which can be attributed to the uniform distribution of both Ni and Cd in the alloy resulting in better mechanical properties. These results were comparable to the ones reported for Cd, Zn–Ni and Ni–Zn–P alloys [27].

Fig. 9. Effect of CdSO$_4$ content on the surface morphology of Zn–Ni–Cd alloys. (Average current density — 4 mA/cm$^2$, duty cycle — 0.1).
deposition metal ions are transferred to the cathode and adatoms are formed by the charge transfer reaction and finally incorporated into the crystal lattice. This phenomenon occurs by building up existing crystals (growth of crystals) or creating new ones (nucleation). These two steps are in competition and can be influenced by the surface diffusion rate of adatom and the rate of charge transfer reaction. High surface diffusion rates, low population of adatoms caused by slow charge transfer reaction and low overpotential lead to the growth of crystals; conversely, low surface diffusion rates, high population of adatoms, and high overpotential increase the rate of nucleation [41]. Since the limiting current density and the overpotential of pulse electrodeposition is always higher than that of DC electrodeposition, pulse deposition causes the nucleation rate to increase which results in uniform distribution of the particles which leads to higher hardness values for the pulse deposited Zn–Ni–Cd than the DC deposited samples. Moreover, the electrodeposition can be carried out at a higher current density by decreasing the pulse periods or by decreasing the duty cycle. Also, better adhesion of the pulse deposited Zn–Ni–Cd alloy with the substrate can be seen from the cross-sectional images.

3.7. Linear polarization, Tafel polarization and OCP studies

The corrosion characteristics of Zn–Ni–Cd ternary alloy deposits were evaluated using Tafel and linear polarization techniques. The linear polarization study was done by varying the potential of the Zn–Ni–Cd deposits by ±20 mV from the open circuit potential at a scan rate of 0.5 mV/s. The potentials mentioned in the study are measured vs. saturated calomel electrode (SCE). The linear polarization resistance ($R_p$) and the Tafel characteristics of Cd, DC deposited Zn–Ni–Cd and pulse deposited Zn–Ni–Cd alloys is presented in Table 3. It is seen that the deposit with high nickel and cadmium percentage (19 and 7% respectively) shows highest polarization resistance of 4056 Ω because of the better barrier properties offered by nickel. The alloy composition with Zn–79%, Ni–18% and Cd–3% measured a polarization resistance of 3549 Ω. This clearly indicates that increased amount of zinc in the alloy leads to more sacrificial property and the deposit with low zinc and high nickel and cadmium contents offers more barrier property towards corrosion protection.

Tafel polarization behavior shown in Fig. 15 indicates that the corrosion current is an order of magnitude smaller for the pulse deposited Zn–Ni–Cd with 7% Cd as compared to the 3% Cd or the DC deposited Zn–Ni–Cd (22% Cd) alloys. The $I_{corr}$ for the Zn–Ni–Cd alloys are smaller when compared to bare Cd ($1.43 \times 10^{-5}$ A/cm$^2$) and Zn–Ni alloys ($3.8 \times 10^{-4}$ A/cm$^2$). The corrosion rates were calculated using the corrosion current and the comparison is shown in Fig. 16. The Zn–Ni–Cd alloys showed lower corrosion rates of 0.49 and 1.03 mpy for 7% and 3% Cd respectively when compared to the DC deposited Zn–Ni–Cd alloys (Cd=22 wt.%) which exhibited a corrosion rate of 2.87 mpy [42]. Approximately six times decrease in the corrosion rate was observed when compared to the DC deposited Zn–Ni–Cd alloy which has 22 wt.% Cd.

The Zn–Ni–Cd alloy with composition 79/18/3 for Zn, Ni and Cd respectively showed an $E_{corr}$ value of −0.857 V vs. SCE due to high amount of zinc. Whereas, the other alloy with Zn/ Ni/Cd composition 74/19/7 showed an $E_{corr}$ value of −0.803 V vs. SCE which is close to that of bare Cd. The shift towards more positive potentials in the latter case is attributed to the increase in both the Ni and Cd content in the deposit. The $E_{corr}$ and $I_{corr}$ values of bare Cd, Zn–Ni, DC deposited Zn–Ni–Cd and the two pulse deposited Zn–Ni–Cd coatings are presented in Table 2.

The variation of $E_{corr}$ vs. time with the composition of Zn–Ni–Cd coating is shown in Fig. 17. It is observed that, the bare Cd deposit has a potential of $\sim −0.770$ V vs. SCE and reached the steel potential after 60 h. The DC deposited Zn–Ni–Cd has a potential of $\sim 0.65$ V vs. SCE and offers sacrificial protection for nearly 90 h beyond which underlying iron was exposed. The initial OCP of pulse deposited Zn–Ni–Cd alloys are $−0.803$ (7% Cd) and $−0.838$ (3% Cd) V vs. SCE and it remained constant throughout the testing (exceeding 100 h) for these alloys. The Zn–Ni alloy with $\sim 7%$ Cd has a positive effect in reducing the corrosion rate by positively shifting the corrosion potential in the test solution.

These results suggest that increasing the zinc content in the deposit results in large potential difference between underlying steel substrate and the deposit. Due to large potential difference, the zinc in the deposit dissolves at a faster rate when compared to the other two alloy compositions with comparatively higher
nickel and cadmium content. These studies emphasize the superior corrosion and sacrificial properties of the pulse deposited Zn–Ni–Cd coatings.

3.8. ASTM B117 salt spray testing

Salt spray testing was performed to evaluate the coating performance under accelerated corroding conditions in a salt spray test chamber whose temperature was set at 35 °C. The samples were exposed to a constant 5% salt fog in accordance with the ASTM B117 specifications. The appearance of the white rust, red rust and the failure of the samples were observed as a function of time. Five percent of red rust on the surface of the samples was defined as the basis for failure criterion. The deposit thickness in all the cases was ∼12 μm. No post treatment or passivation was provided on the surface of the coatings. Pulse deposited Zn–Ni–Cd samples with 3 and 7 wt.% Cd were tested under these conditions. Visual observations were made after taking out the panels at regular intervals and the results are shown in Table 4. Prior to visual observation, the test panels were washed in cold water and dried under flowing air. It can be seen from the table that the first white rust formation was observed after 144, 240 and 282 h of exposure for 22 wt.% Cd (DC), 3 wt.% Cd (pulse) and 7 wt.% Cd (pulse) containing Zn–

Fig. 11. Effect of CdSO₄ content on the surface morphology of Zn–Ni–Cd alloys. (Average current density — 6 mA/cm², duty cycle — 0.1).

Fig. 12. Depletion of cadmium content with number of deposition at different CdSO₄ concentration.
Ni–Cd alloys respectively. These values are far better than the values reported in the literature for Cd and Zn–Ni alloys without passivation [17]. The red rust formation was further prolonged for DC deposited and pulse deposited Zn–Ni–Cd alloys when compared to bare Zn–Ni alloys with 15% Ni. The first red rust spots were noticed after 576 and 744 h for 3 wt.% Cd and 7 wt.% Cd containing Zn–Ni–Cd alloys respectively. The ASTM B 117 study further supports the better corrosion protection property of pulse plated Zn–Ni–Cd alloys with low cadmium content.

4. Conclusion

A novel pulse electrodeposition process was developed to deposit Zn–Ni–Cd ternary alloys on carbon steel substrate using an alkaline bath. Experimental results indicated an increased average current density resulted in a decrease in both nickel and cadmium content and an increase in the zinc content. The highest nickel and cadmium content (19 and 7 wt.% respectively) was obtained when an average current density of 300 mA cm⁻² was used. The polarization resistance of the coatings increased with an increase in the cadmium content. The corrosion resistance was found to be enhanced with an increase in cadmium content. The EDAX analysis of cadmium showed a uniform distribution of cadmium in the coating. The X-ray diffraction patterns showed the presence of Zn, Ni, and Cd peaks in all coatings. The mechanical properties of the coatings showed good adhesion and hardness with a hardness value of 215.18 VHN100gf for 74 wt.% Cd containing alloy. The cross-sectional BSEM images showed a uniform coating with a thickness of 5 µm. The corrosion rate was found to be low with a corrosion rate of 0.49 mpy for 74 wt.% Cd containing alloy. The overall results indicate that pulse plated Zn–Ni–Cd ternary alloys with low cadmium content offer better corrosion protection compared to DC plated alloys.
density of 4 mA/cm² was used. Increase in particle size of the deposit was observed with the increase in the average current density. For short $T_{on}$ times, higher percentage of zinc and cadmium was deposited. Salt spray tests and electrochemical corrosion techniques revealed excellent corrosion protection properties of pulse deposited Zn–Ni–Cd alloys suggesting that this alloy is a better alternate to the conventional cadmium coatings.

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