

Development of Zn-Co alloy coatings by pulsed current from chloride bath

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Zinc-M (where M = Ni, Co and Fe) alloy is of great interest owing to their better mechanical and corrosion properties compared with pure zinc coatings. Corrosion resistance of Zn-Co alloy coatings can be improved considerably by pulse plating. The paper details the optimization of Zn-Co alloy bath using pulsed current and details the superiority of pulse plating over direct current plating. Electroplating of Zn-Co alloys over mild steel was carried out under different conditions of pulse parameters like duty cycle, frequency and peak current density. The production and properties of the deposits were found to be influenced by pulse parameters employed. Within the ranges studied, the bath follows anomalous codeposition with preferential deposition of less noble zinc. The influence of current density on %wt. of Co in the deposit and cathode current efficiencies was studied. It was observed that the deposit at average current density of 5.0 A.dm^{-2} , 50% duty cycle and 100 Hz frequency showed excellent corrosion resistance with fine structure. The peak performance of pulse electrodeposit against corrosion was attributed to the change in the surface homogeneity as evidenced by scanning electron microscope (SEM) image. The drastic decrease of corrosion rate in pulse electrodeposit was attributed to the formation of semiconductor films on the surface as supported by impedance spectroscopy signals.

Keywords: Zn-Co alloy, Electrodeposition, Pulse plating, Corrosion, SEM

To achieve the desired level of corrosion protection to steel to endure severe corrosive environment, zinc plating ($\sim 25 \mu\text{m}$ thick) or zinc-M (where M = Ni, Co and Fe) alloy coatings is required. The major disadvantages of using thick coatings are the poor formability and weldability^{1,2}. Also, a thick coating makes it difficult to achieve a smooth finish after painting³. This has led to the development of thinner electrodeposited coatings with improved properties compared with zinc. Therefore, extensive attempt had been taken recently to develop high corrosion resistant coating on steel and as a result, the conventional Zn coatings being replaced by Zn alloys⁴⁻⁹. Alloys of zinc with metals of Fe group (Fe, Ni, Co) have been considered as prime candidates for this purpose. Of the several zinc alloys available, some researchers believe that Zn-Co alloy coatings are the most promising ones for the substitution of zinc coatings in the automobile industry because, with a small cobalt addition ($<1 \text{ wt.}\%$), it is possible to obtain better corrosion resistant coatings, similar to Zn-Ni (10-14 wt.%)¹⁰. The deposits of Zn-Co alloys with cobalt content of more than 6 to 7 wt.% have not been widely reported^{11,12}. This may be due to the perceived limitations arising from anomalous codeposition¹³, since the preferential deposition of zinc has been

observed under a wide range of conditions, while the content of noble element cobalt in the deposit was much less than that in the bath^{14,15}.

Several hypotheses have been advanced to explain anomalous codeposition of alloys. The ideas are focused on phenomena occurring on the cathode surface. Higashi *et al.*¹⁶ and Decroly^{17,18} proposed the hydroxide suppression mechanism to explain the anomalous codeposition of Zn-Co alloy in a sulphate bath. The discharge of cobalt is inhibited by the formation of a zinc hydroxide film that offers resistance to the transport of the Co^{2+} ions¹². The electrodeposition of Zn-Co alloys with controlled morphology and composition has been the subject of many studies as a consequence of their observed improved corrosion resistance and catalytic activity^{19,20}. These two completely different functions of the alloy require different morphologies and compositions. The electrodeposition process using pulsed current (PC) favours the control of these two deposit characteristics because three parameters can be varied independently- the peak current density, the on-time and the off-time²¹, whereas in the direct current (DC) only the current density can be changed. Fei and Wilcox²² studied electrodeposition of alloys with pulse and reverse current, they reported that the surface microstructure of the Zn-Co alloy deposits

depends mainly on the average current density and the value of the reverse pulse fraction. Tomachuk *et al.*²³ reported that the morphology of the pulse plated Zn-Co alloy deposits depends mainly on the average c.d. and off-time.

The fact that the production and properties of electrodeposits can greatly be influenced by pulse plating is the driving force of the present work. The advents of pulse plating were tried to explore in optimization of acid chloride bath of Zn-Co alloy for peak performance of its coatings against corrosion. The composition and morphology of deposited alloys were analyzed as a function of the PC parameters and compared with those obtained by using DC. The average c.d. in the present study was chosen such that it is in the same range as employed in DC deposition.

Experimental Procedure

Electrolyte was prepared using LR grade chemicals and distilled water. The *pH* of the bath was maintained at 4.0 and was monitored frequently and adjusted to 4.0 with HCl. Deposition was carried out using stationary parallel planar electrodes with pure zinc anode and a mild steel cathode. After deposition, the cathode was washed with tap water and rinsed with distilled water and dried. Zn-Co alloy plating bath was optimized using glycine and gelatin as brighteners using conventional Hull cell. The bath composition and operating parameters of optimized bath for deposition of bright and smooth Zn-Co alloy are given in Table 1. The corrosion resistance of

Zinc Chloride	0.59
Cobaltous Chloride	0.03
Potassium chloride	0.94
Ammonium chloride	1.40
Glycine	0.09
Gelatin	10 g/L
<i>pH</i>	4.0
Temperature (K)	303
c. d. (A dm ⁻²)	5.0
Anodes	Pure zinc

Zn-Co alloys was tried to improve further by PC plating using the same bath. Pulse plating was carried out at constant temperature of 303K with pulse frequency ranging from 25 to 250 Hz and duty cycle ranging from 10-80%. The duty cycle, frequency and peak current density employed in the present study to meet average c.d. of 5.0 A.dm⁻² are as shown in Table 2. Corrosion behaviour of deposits was studied by electrochemical techniques using Metrohm PGSTAT30 electrochemical work station. The polarization measurements were performed at 298 ± 1 K in stagnant aerated 5% NaCl solution at *pH* 6 (ASTM B117) using saturated calomel electrode as reference and platinum as counter electrode. Corrosion rates of the electrodeposited Zn-Co deposits were studied by Tafel method at a scan rate 1.0 mV/s. Electrochemical impedance spectroscopy (EIS) was used to evaluate the barrier film resistance of Zn-Co deposits in frequency range of 20 mHz-100 KHz. The composition of deposit was determined by spectrophotometric method at 480 nm²⁴ by stripping the deposit in dilute HCl using inhibitor. Variation in surface morphology of the deposits with duty cycle was studied using scanning electron microscopy (SEM).

Table 1 — The bath composition and operating parameters of optimized bath for deposition of smooth Zn-Co alloy

Constituent	Optimized bath composition (M)
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Results and Discussion

Effect of on-time and average c.d. on %wt. of Co

The influence of current on-time (T_{on}) on the amount of Co in the alloy deposit is shown in Fig. 1. It was found that the %wt. of Co in the deposit

Table 2 — The duty cycle, frequency and peak current density employed for deposition of Zn-Co alloy to meet average c.d. of 5.0 A.dm⁻²

Duty cycle	Pulse frequency (Hz)					Current density (A.dm ⁻²)	
	25	50	100	150	250	Peak	Average
	Pulse on-off time (ms)						
10	4.0-	2.0-	1.0-	0.7-	0.4-	50.0	5.0
20	36	18	9.0	6.0	3.6	25.0	5.0
50	8.0-	4.0-	2.0-	1.7-	0.8-	10.0	5.0
80	32	16	8.0	5.0	3.2	6.25	5.0
	20-	10-	5.0-	3.35-	2.0-		
	20	10	5.0	3.35	2.0		
	32-	16-	8.0-	5.0-	3.2-		
	8.0	4.0	2.0	1.7	0.8		

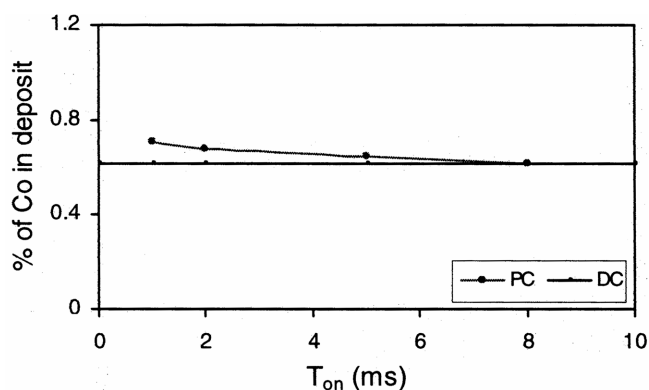


Fig. 1 — Variation of %wt. of Co during PC plating with current on-time (T_{on}) against to its value during DC plating

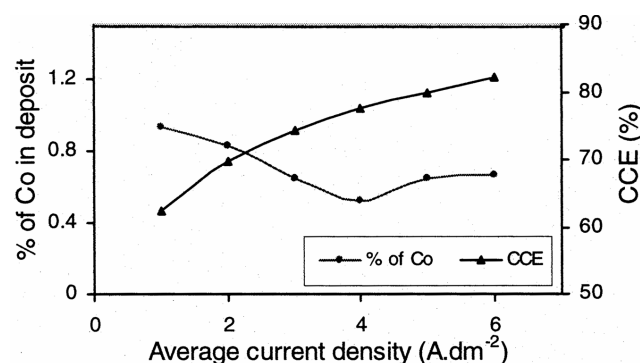


Fig. 2 — Change in the deposit Co content and cathodic current efficiency as a function of the average current density

decreased gradually with the increase of on-time and it tends to reach the value during DC plating at high on-time. Highest cobalt content (0.71%) was found at 10% duty cycle and it decreased gradually with increase of duty cycle at constant frequency of 100 Hz. This may be attributed to the increased depletion of nobler Co at cathode film. Figure 2 shows the variation of %wt. of Co in Zn-Co alloy deposits with average current density (I_{av}). It was observed that %wt. of Co in the deposit decreases with increase of c. d. at first and it tends to increase at high c.d. region. This increase of %wt. of Co at high c.d. is due to the rapid depletion of more readily depositable metal (Zn) at the cathode surface. Effect of cathode current efficiency (CCE) with average current density was also studied and was found to show a direct dependency with c.d. as shown in Fig. 2.

Effect of duty cycle and frequency on wt. % of Co

The effects of duty cycle (θ) on %wt. of Co in the deposit were studied in the frequency range of 25-250 Hz and duty cycle range of 10-80% and are shown in Fig. 3 and Table 3. It was found that %wt.

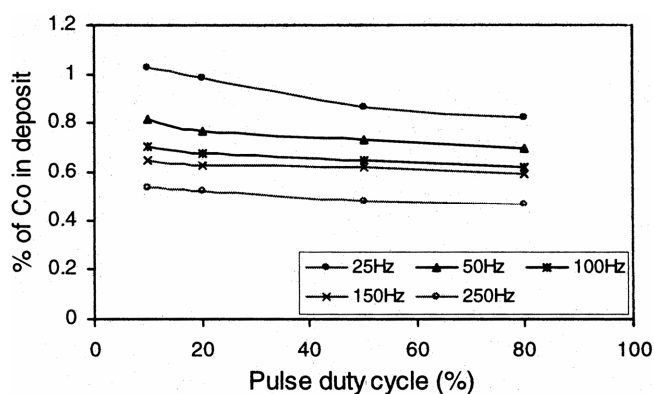


Fig. 3 — Effect of pulse duty cycle at various frequencies on %wt. of Co in the deposit from optimized average c.d.

Table 3 — Influence of pulse duty cycle and pulse frequency on wt.% of Co in the deposit of Zn-Co alloy at 303 K

Duty cycle (%)	Frequency (Hz)					Nature of the deposit
	25	50	100	150	250	
	Wt.% of Co in the deposit					
10	1.026	0.817	0.708	0.652	0.535	Semi bright
20	0.983	0.764	0.679	0.626	0.520	Bright
50	0.866	0.731	0.646	0.621	0.480	Bright
80	0.826	0.699	0.621	0.596	0.465	Bright

of Co in the deposit do change with frequency and duty cycle also. It was seen that the %wt. of Co in the deposit decreased with the increase of duty cycle in entire frequency range. At a frequency of 25, the %wt. of Co in the deposit decreased from 1.026 to 0.535 as the frequency increased from 25 Hz to 250 Hz. Further, the %wt. of Co in the deposit was found to decrease with increase of duty cycle. This is due to the increased peak current density (I_p) at low duty cycle according to $I_p = I_{av}/\theta$, and because of high I_p at $\theta = 10\%$ due to increased depletion of preferentially depositable zinc at cathode. It was observed that in all conditions of pulse parameters the %wt. Co in the deposit did not exceed more than 1.026%. This is attributed to the perceived limitations arising from anomalous codeposition as characterized by Zn-Fe group metal alloys¹³.

Effect of duty cycle and frequency on thickness of deposit

It was observed that the duty cycle and frequency have great influence on the thickness (μm) of the deposit over the entire range of frequency (Fig. 4). The thickness of Zn-Co deposit increased almost linearly with increase of both deposition times (T_{on})

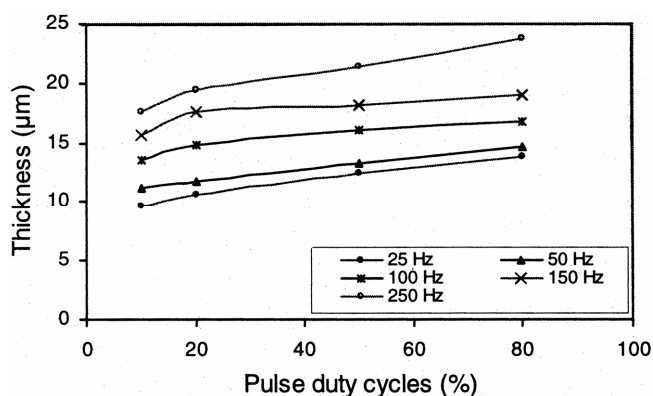


Fig. 4 — Variation in the thickness of the deposit with duty cycle and frequency

and the pulse frequency. This indicates that the deposition of Zn-Co will always proceed with the processing time and the peak current density. The thick deposit at higher duty cycle and frequency was found to be more porous and flaky due to likely evolution of hydrogen at cathode.

Since the deposit was found to be very smooth and uniform at duty cycle (θ) = 50% this was fixed as optimized duty cycle. The effect of frequency on %wt. of Co and CCE was studied keeping 50% duty cycle. The effect of frequency on the chemical composition and CCE of Zn-Co alloy deposit is shown in Fig. 5. It was found that %wt. of Co decreased as the pulse frequency increased which may be ascribed by decrease of relaxation time and depolarization of the cathode. At very low frequency, the relaxation time being very high more readily depositable zinc being more depleted makes nobler cobalt to deposit. But at high frequency the relaxation time being very low, not much depletion of zinc ions at the cathode surface takes place and the deposit has less %wt. of Co. The Zn-Co electroplate obtained at frequency of 100 Hz and 50% duty cycle was found to be very smooth and bright and was fixed as optimized pulse parameters for temperature variation.

Effect of temperature

The effect of temperature on wt.% of Co in the deposit and CCE was studied in the range of 283-323 K at optimum conditions like duty cycle (50%), frequency (100 Hz) and average current density of 5.0 A.dm^{-2} . The variation of wt.% of Co with temperature is shown in Fig. 6 and it reveals that cobalt content in the deposit is a function of plating temperature. Further, the increase of less noble metal (zinc) in the deposit with increase of temperature supports the fact that electrolytic bath follows anomalous codeposition¹³. Cathode current efficiency was found to increase with increase of temperature up to 323 K then it decreases slowly. This increase of CCE with temperature is due to rapid replenishment of Zn^{+2} ions at cathode diffusion layer and it tends to maximum towards high temperature (Fig. 6).

Corrosion behaviour of Zn-Co alloy

Tafel studies

The corrosion behaviour of pulse plated Zn-Co alloys under different conditions of duty cycle at optimum frequency and average current density was evaluated using Tafel polarization method (Fig. 7). The open circuit potentials (OCP) of all Zn-Co alloys were found to be more negative than that of steel base which indicates that the Zn-Co alloy deposits offer sacrificial protection to the base metal. It was found that the electrodeposits using pulsed current offers better corrosion resistance compared to DC deposit (Table 4) and is attributed to the change in kinetics of the hydrogen evolution reaction on pulse deposits. Further, polarization curve at 50% duty cycle was found to exhibit highest corrosion resistance compared to that at other duty cycles. The results of variation of corrosion rate with frequency are shown in Fig. 8. It was found that frequency plays a crucial role in corrosion performance of the deposit. The corrosion results indicate that wt.% of Co in the alloy is not only the factor responsible for good corrosion resistance, surface morphology controlled by pulse parameters also play important role.

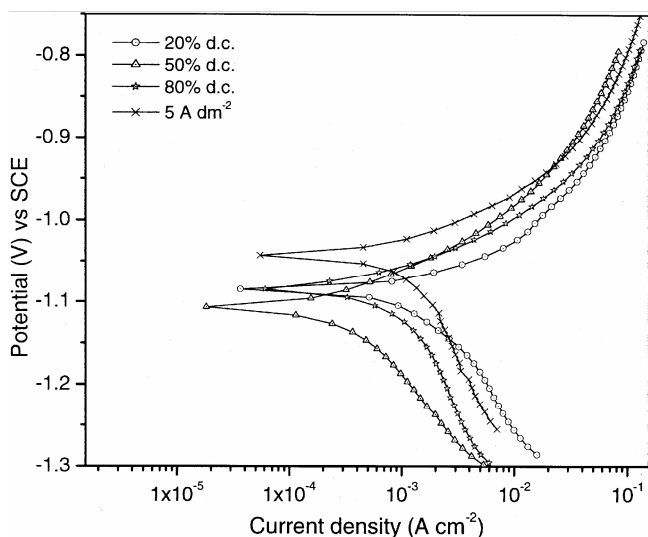


Fig. 7 — Potentiodynamic polarization curves for Zn-Co alloy coatings recorded after exposure in 5% NaCl at different duty cycle at optimized frequency and average c.d.

Table 4 — Corrosion current, corrosion potential and corrosion rate of Zn-Co alloy deposits obtained by pulse plating

Duty cycle (%)	E_{corr} (Volts)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	Corrosion rate (mm/y)
10	-1.083	24.89	0.3693
20	-1.080	16.46	0.2442
50	-1.100	13.49	0.2002
80	-1.102	24.58	0.3177
5.0 A.dm ⁻² (DC)	-1.040	33.25	0.4763

Electrochemical impedance spectroscopy (EIS)

The electrochemical behaviours of electrodeposited Zn-Co alloys were studied using impedance spectroscopy. Figure 9 presents the comparison of Nyquist responses obtained for Zn-Co alloy deposits under different conditions of duty cycle. The improved corrosion resistances were exemplified by the barrier properties of the coatings obtained using pulsed current. Zn-Co alloy obtained with optimized pulse parameters were found to show least corrosion rate with barrier properties of the deposits. The electrical equivalent of the electrified double layer for optimized deposit is given in the Fig. 10. Nyquist plots are found to be not perfect semicircles as expected from the theory of EIS for the assumed equivalent circuit, and this difference can be explained as follows. The Nyquist plots obtained in the real system represent a general behaviour where the double layer on the interface of the metal/solution does not behave as a real capacitor. On the metal side, electrons control the charge distribution whereas on

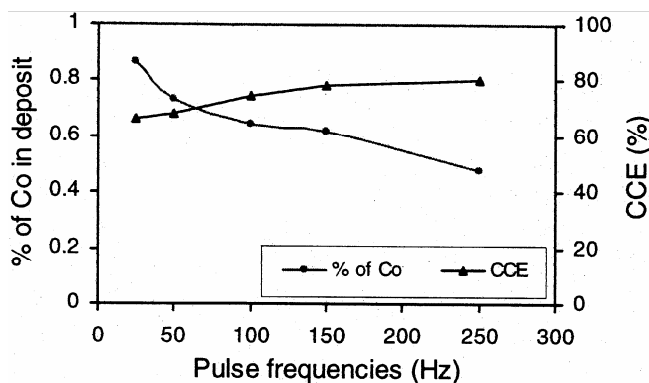


Fig. 5 — Change in the %wt. Co and cathode current efficiency (CCE) of the deposit as a function of frequency at 50% duty cycle

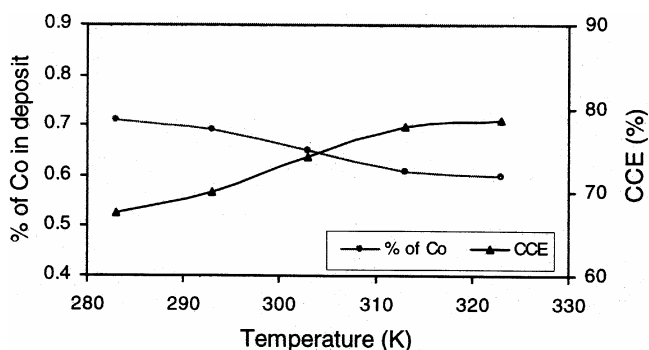


Fig. 6 — Change in the % wt. of Co and current efficiency as a function of bath temperature

the solution side it is controlled by ions. Since ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer²⁵. The deposit obtained at 50% duty cycle and 100 Hz

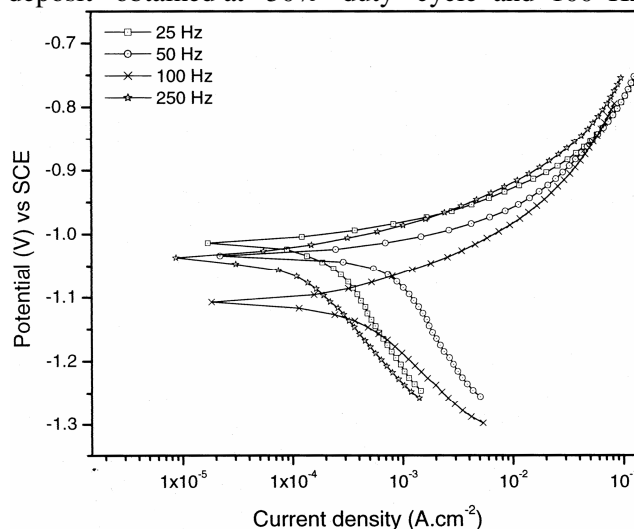


Fig. 8 — Potentiodynamic polarization curves of pulse plated Zn-Co alloys at various frequency recorded after exposure in 5% NaCl at optimum duty cycle and average c.d.

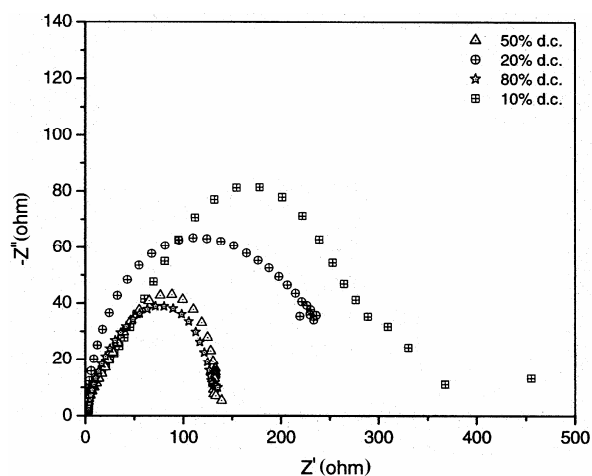


Fig. 9 — Electrochemical impedance spectroscopy of pulse plated Zn-Co alloys at different duty cycle and optimized frequency and average c.d.

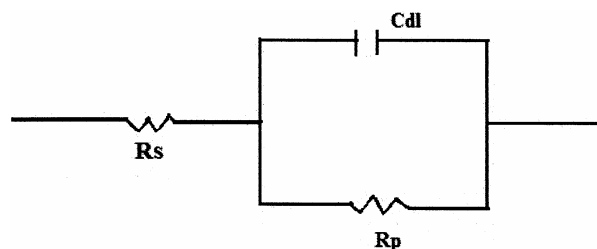
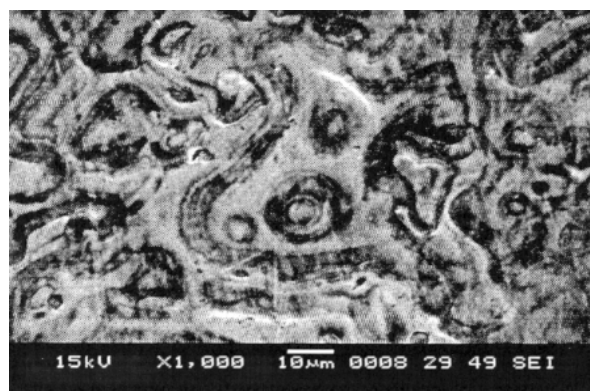
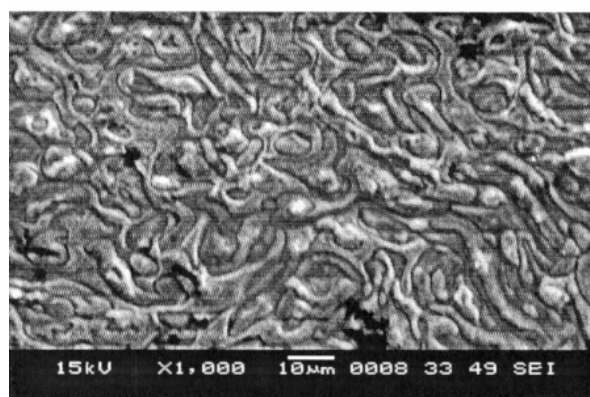


Fig. 10 — Electrical equivalent of electrified interface of Zn-Co alloy deposited from the optimized bath

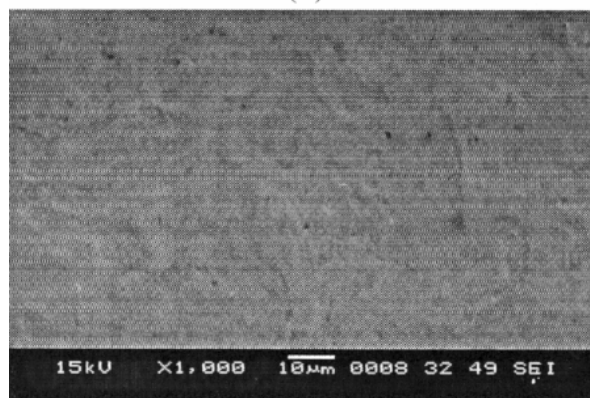
frequency is found to be more corrosion resistant than any other deposits and this improved corrosion resistances were exemplified by the barrier properties of the coatings obtained using pulsed current.



(a)



(b)



(c)

Fig. 11 — SEM micrograph of Zn-Co deposit obtained at (a) 5 A.dm^{-2} by direct current (b) 10% duty cycle at 100 Hz and (c) 50% duty cycle at 100 Hz.

SEM analysis

Surface topography of Zn-Co deposits on mild steel surfaces are shown in Fig. 11. The deposit obtained using direct current was found to be very rough and non uniform [Fig. 11(a)]. It was observed that the surface morphology of the deposits has changed drastically with pulsed current. Further, the grain size of the deposit decreased as the duty cycle increased and the deposit obtained at 50% duty cycle is found to

be the most homogeneous and uniform compared to those obtained at 10% duty cycle [Fig. 11(b) and 11(c)]. It was found that morphology of the deposits does not depend mainly on the wt.% of cobalt content of the deposit but on the average current density and duty cycles.

Conclusions

A pulse plating bath has been proposed for deposition of smooth and uniform Zn-Co alloy over mild steel. Pulse plating have been used to enhance the corrosion resistance of electrodeposited Zn-Co alloys for better industrial applications. Effective control of the zinc-cobalt ratio in the alloy coatings was achieved by proper simulation of pulse parameters. The appearance and corrosion performance of the deposit has been found to be a function of its composition. The bath temperature had a very strong influence on the chemical composition of the deposit. Though corrosion resistance of Zn-Co alloy was affected by wt.% Co in the deposit, it is more influenced by pulse variables such as frequency and duty cycle. Hence, it was concluded that wt.% Co is not the sole criteria for good corrosion resistance but also the grain size of the deposit. Zn-Co alloy deposit by pulsed current showed superior corrosion protection compared to direct current deposit. The decreased %wt. of Co in the deposit with increase of pulse frequency may be ascribed by decrease of relaxation time and depolarization of the cathode. At very low frequency, more readily depositable zinc being more depleted makes nobler cobalt to deposit. Pulse variables (i.e. 50% duty cycle, 100 Hz frequency and 5.0 A.dm⁻²) have been proposed for electrodeposition of smooth and uniform Zn-Co alloy over steel for best performance against corrosion. Compared to the deposits obtained using direct current, a homogenous and fine grained deposit could be obtained by using pulsed current. Compared with DC data, the Zn-Co alloy deposited by pulse current gave superior corrosion protection.

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