Influence of 2-methyl-5-nitro-N-phenylmethylidene aniline (CP_1) on Zn-Mn alloy plating from acid sulphate bath

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Abstract

The influence of condensation product (CP1) of 2-methyl-5-nitroaniline and salicylaldehyde on Zn-Mn alloy electrodeposited onto mild steel was studied in acidic sulphate bath. The bath constituents were optimized through Hull-cell experiments. The morphology and composition of the deposits depends on the current density, temperature, bath composition and additive concentration. The results showed that the additives modifies the structure and surface morphology of the deposit to a greater extent. The operating parameters such as pH, temperature and current density were also optimized. The current efficiency and throwing power were measured at different current densities. Polarization study was carriedout under galvastatic conditions. The consumption of brightener was determined in the laboratory scale. SEM photomicrographs revealed the fine-grained structure of the deposit. The deposited phases were analyzed by X-ray diffraction method. The IR spectrum of the scraped deposit confirmed the inclusion of addition agent into the deposit.

Key words: Condensation product, Hull-cell studies, Manganese sulphate, Sulphate bath, Zinc sulphate

1. Introduction

Electrodeposited zinc coatings are widely used for the protection of steel structures. Many studies have been undertaken in order to improve the durability of zinc coatings.[1-3] Various Zn-based alloys Zn-Ni, Zn-Co and Zn-Fe are currently used in industry. Several authors,[4-6] have also investigated the Zn-Mn alloys. In review article, Wilcox reported [7-8] the results obtained by several corrosion studies and concluded that the corrosion resistance in laboratory chloride environments is superior to zinc and other zinc alloys. The ability of Zn-Mn alloys to resist atmospheric corrosion was tested [9] who reported a significant improvement of their Zn-Mn alloy in a marine atmosphere in comparison with Zn or other Zn alloys. Several studies have shown that the coatings composed of e-Zn-Mn the phase ensured the best protection ability. [10,11]

Zinc alloy deposition has been interest recently since these alloys provide better corrosion protection than pure zinc coating.[12,13] It is known, in particular that the mechanical, physical and electrochemical properties can be improved by alloying zinc with manganese.

Gabe and coworkers have reported that Zn-Mn alloy with a manganese content of approximately 30% shows the highest corrosion resistant. This highest corrosion resistance is associated with monophasic structure of the coating.[14] Studied the influence of bath composition on the corrosion behavior of Zn-Mn coating and reported that alloys with manganese contents around 11% had high corrosion resistance due to their monophasic structure.

In the present work, efforts have been made to develop a bath solution containing a single addition agent, which is easily soluble in water and increases the deposition potential. It is known that the condensation product of aldehydes and amines are good brighteners than single aldehydes or amines in the bath solution. This may be due to the presence of electroactive >C = N group in the molecule. Various amines and aldehydes were subjected to condensation reaction [15,16] and used as addition agent in basic zinc sulphate bath. Among these, the condensation product formed

between 2-methyl-5-nitro aniline and salicylaldehyde is found to be an addition agent effective addition agent for getting good deposit.

2. Experimental

The chemicals used were of AR grade and easily soluble in water. For the preparation of solution distilled water was used. All the experiments were carried out at room temperature. The pH of the solution was maintained and adjusted by dil sulfuric acid or sodium carbonate solution. Zinc metal plate of 99.99% was used as Anode and polished steel specimen was used as cathode

The Hull-cell experiments with the bath solutions were carried out at 2 A cell current for 10 min, given in table.1. The total volume of Hull-cell was 267 mL with an anode dimension 6 cm ´ 6.5 cm (zinc metal). The anode was activated each time by immersing in 10% HCl followed by water wash. The cathode dimension 10 cm ´ 7.5 cm (mild steel) of standard Hull-cell size were mechanically polished to obtained smooth surface and degreased by dipping in boiling trichloroethylene. The scales and dust on steel plates were removed by dipping in 10% HCl solution.

Table 1. Basic bath composition and operating condition

Bath composition	Quantity (gL^{-1})	Operating conditions
$ZnSO_4 \times 7H_2O$	200	Anode: zinc metal (99.99%)
$MnSO_4 \times H_2O$	8	pH: 3. Plating time: 10 min
Na_2SO_4	60	Cathode: mild steel
H_3BO_3	16	Temperature: 293-303 K
CTAB	2	Cell current: 2 A

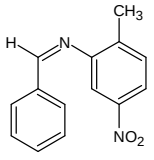
Then these steel plates were washed with water and used for the experiments as such. After the plating experiment, the plates were subjected to bright dip in 1% nitric acid for 2-5 sec followed by water wash. The nature and appearance of zinc deposit was carefully studied and recorded through the Hull-cell codes (Figure (a)).

All the experiments were conducted at 303 K. A known amount of condensation product was added to the plating bath; the bath solution was stirred for 30 min and then used for Hull-cell experiments. Condensation product was synthesized from equimolar amounts of 2-methyl-5-nitroaniline (1 g) with chemical formula, $C_7H_8N_2O_2$ and salicylaldehyde (0.70 mL) with chemical formula, $C_7H_6O_2$ in ethanol and acetic acid medium (20 + 20 mL), under reflux conditions for 3 h at 343 K. The completion of the reaction was tested with TLC. The resulting dark red product was diluted to 100 mL with distilled water and a known amount of this solution was added to the electroplating bath solution.

Polarization studies were carried out by using a three compartment cell. The area of zinc anode was 2 cm^2. Mild steel was used as cathode with an exposed area of 2 cm^2. The cathode potential was recorded galvanstatically with respect to saturated calomel electrode, at different current densities.

Haring and Blum cell was used to measure the throwing power of the bath solution and a rectangular methacrylate cell was used to measure current efficiency. For throwing power measurement the current distribution ratio between anode and cathode was 1:5. For determining consumption of brightener, a rectangular cell of 2.5 mL capacity was used.

IR spectrum the scraped deposit was taken to ascertain the inclusion of addition agents. SEM photomicrographs were taken to ascertain the nature of deposit in the presence of addition agents.



2-methyl-5-nitro-*N*-[(1*Z*)-phenylmethylidene]aniline

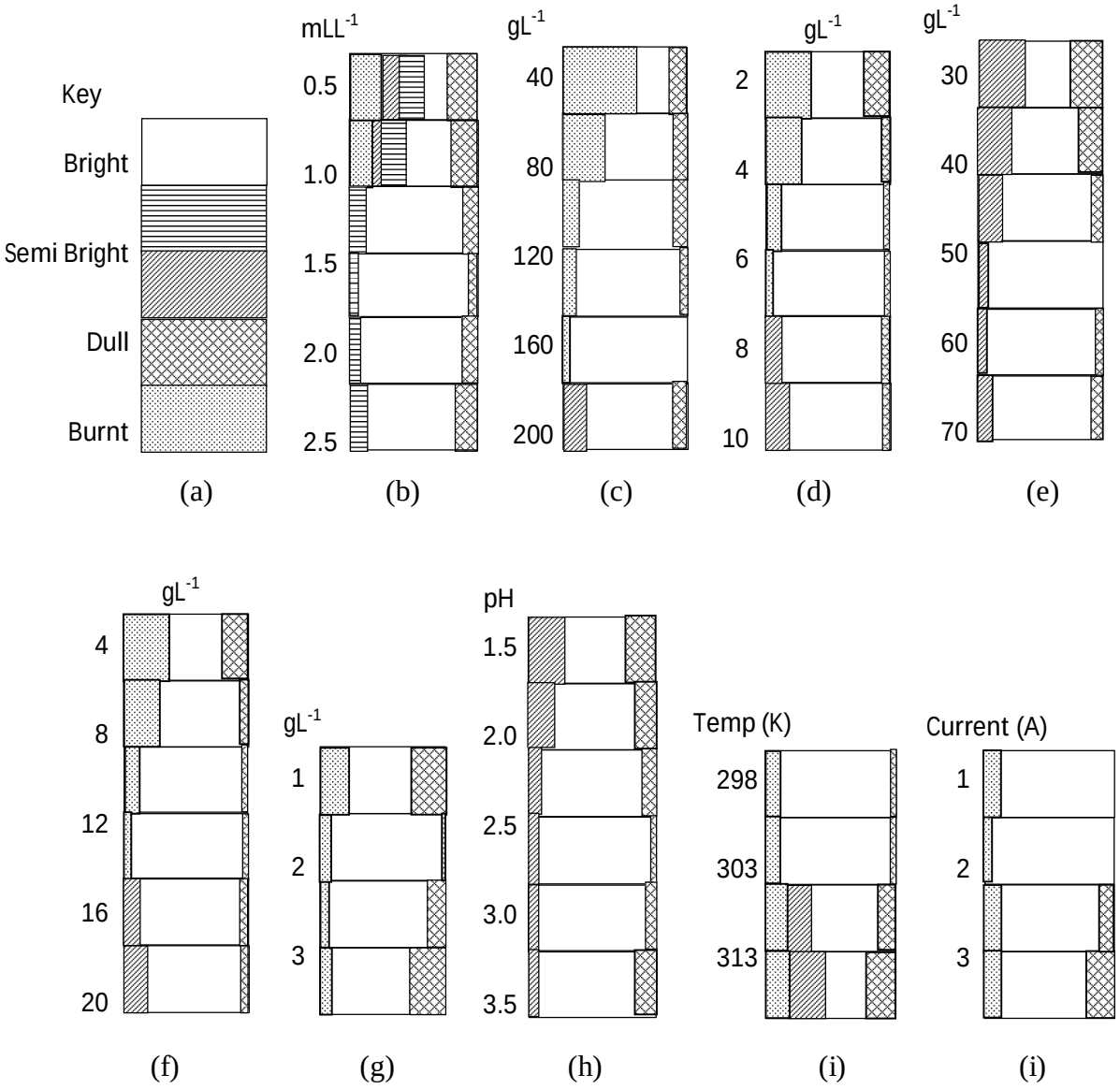


Figure 1 : Hull-cell figures (a) key (b) CP1 (c) ZnSO4 (d) MnSO4 (e) Na2SO4 (f) H3BO3 (g) CTAB (h) pH (i) temperature (j) cell current.

3. Results and Discussion

3.1 Hull Cell Studies

3.1a Effect of condensation product

The Hull cell experiments with basic bath solution containing zinc sulphate, sodium sulphate, boric acid and CTAB gave coarse dull deposit between the current density range of 1 and 6 A dm^{-2}. To improve the nature of the deposit condensation product formed between 2-methyl 5-nitroaniline (AR Grade sd. Fine chemicals) and salicylaldehyde (AR Grade sd Fine chemicals) was added to the bath solution. The condensation product was prepared by mixing 1g of 2-methyl-5-nitro aniline and 0.70 mL of salicylaldehyde in water (ethanol and acetic acid mixture) and the resultant solution was refluxed for 3 h at 343 K. The resulting dark red product was diluted to 100 mL with distilled water and a known amount of this solution was added to the basic bath solution. At lower concentration of the condensation product, the deposit was semi- bright between the current density range of 1 and 6 A dm^{-2} at low current density region dull and at high current density region burnt deposit was obtained. With increase in the concentration, the nature of deposit was improved and at a concentration of 8 mL of the condensation product given in table.2 the Hull-cell panels were bright between the current density range 1 and 8 A dm^{-2}. Further increase in the concentration of condensation product the bath gave dull deposit in the high current density region. Based on the above results, the

concentration of condensation product was kept at 8 mL as optimum (Figure 1 (b)).

Table 2. Optimum bath composition and operating conditions

Bath composition	Quantity (gL^{-1})	Operating condition
$ZnSO_4 \times 7H_2O$	200	Anode: zinc metal (99.99%)
$MnSO_4 \times H_2O$	8	pH: 3.0 Plating time: 10 min
Na_2SO_4	60	Cathode: mild steel
H_3BO_3	16	Temperature: 293-303 K
CTAB	2	Cell current: 2 A
Optimum concentration of (CP_1)(mLL^{-1})	8	

3.1b Effect of zinc sulphate

To find out the effect of zinc metal ion concentration, zinc sulphate concentration was varied from 40-240 g at lower concentration of zinc sulphate bright deposit was observed in the current density region 0.5 and 3 A dm^{-2}. At low current density region uncoated and at high current density region burnt deposits were obtained. With increase in the concentration of zinc sulphate the brightness was extended to lower and higher current density regions. At concentration of 200 gL^{-1} satisfactory bright deposit was obtained in the current density range 1-8 A dm^{-2}. With further increase in the concentration of zinc sulphate no improvement in the nature of the deposit was observed. The concentration of zinc sulphate was fixed at 200 gL^{-1} as optimum (Figure 1(c)).

3.1c Effect of manganese sulphate

The manganese sulphate concentration was varied from 2 to 12 gL^{-1} by keeping zinc sulphate at 200 gL^{-1} sodium sulphates at 60 gL^{-1} Boric acid at 16 gL^{-1} and CTAB 2 gL^{-1} respectively. At lower concentration of manganese sulphate bright deposit was observed in the current density range between 1 and 8 A dm^{-2}. At low current density region uncoated and at high current density region burnt deposits were obtained. With increase in the concentration of manganese sulphate the brightness range was extended to lower and higher current density regions. At a concentration of 8 gL^{-1} satisfactory bright deposit was obtained in the current density range 1-8 A dm^{-2}. With further increase in the concentration of manganese sulphate no improvement in the nature of deposit was observed. The concentration of manganese sulphate was fixed at 8 gL^{-1} in bath solution (Figure 1(d)).

3.1d Effect of sodium sulphate

Sodium sulphate was added to increase the conductivity of the bath solution. The Hull-cell patterns showing the effect sodium sulphate are shown in (Figure 1(e)) the concentration of sodium sulphate was varied from 30-80 gL^{-1} at lower concentrations, the Hull-cell panels suffer burnt deposit at high current density region and dull at low current density region. The burnt and dull deposits were found to be reduced and at 60 gL^{-1} of sodium sulphate in the bath solution, the deposit was bright in the current density range 1-8 A dm^{-2}. Further increase in the concentration of sodium sulphate had no effect on the nature of the deposition. Therefore the concentration of sodium sulphate was fixed at 60 gL^{-1} in the bath solution (Figure 1(e)).

3.1e Effect of boric acid

A boric acid buffer solution will maintain a pH range of 8-10, the addition of boric acid to the electroplating bath is to control the variation of H^+ ion concentration in the bath solution. The concentration of boric acid was varied from 4-24 gL^{-1} keeping the concentration of zinc sulphate and sodium sulphate at 200 gL^{-1} and 60 gL^{-1} respectively. Lower concentration of boric acid (4-8 gL^{-1}) gave bright deposit at low current density region. Higher concentration of boric acid gave mirror bright deposit in the current density range 0.5-8 A dm^{-2}. The concentration of boric acid was fixed at 16 gL^{-1} as optimum in the bath solution (Figure 1(f))

3.1f Effect of CTAB

The concentration of CTAB was varied from 1-4 gL^{-1} At low concentration of CTAB, the nature

of the deposit was observed in the current density range between 1 and 6 A dm^{-2}. In the low current density region, dull and at high current density region burnt deposits were obtained. With increase in the concentration of CTAB from 1-2 gL^{-1} satisfactory bright deposit was obtained in the current density range of 1-8 A dm^{-2} at 2 A cell current. With increase in the concentration above 2 gL^{-1} no change in the nature of the deposit was observed. Therefore the concentration of CTAB was fixed at 2 gL^{-1} as optimum in the bath solution (Figure 1(g)).

3.1g Effect of pH

The solution was varied from 2 to 5, at lower pH between 2-2.5 the Hull-cell patterns showed an uncoated area in the low current density region. At pH 3.0 satisfactory bright deposit was obtained in the current density range 1-8 A dm^{-2}. With an increase in pH above 3.0 no deposit was noticed in the low current density region. By these observations the pH of the bath solution was fixed at 3.0. The effect of pH on the deposit nature is shown in (Figure 1(h)).

3.1h Effect of temperature

To see the effect of temperature on Hull-cell experiments, the plating experiments were carried out in a thermostat. The temperature of thermostat was varied from 293-323 K. The deposition was bright in the current density range between 1 and 8 A dm^{-2} at 2 A cell current at a temperature less than 303 K. Above 303 K the deposition was dull in low current density range. So the optimum temperature range was 293-303 K (Figure 1(i))

3.1i Effect of cell current

The Hull-cell experiments were carried out at different cell currents (1-3 A) for 10 min using optimum bath solution. The Hull-cell patterns are shown in (Figure (j)). It was found that at a cell current of 1 A, the deposit was bright in the current range of 0.5-4 A dm^{-2}. At a cell current of 2 A, the deposit was bright in the current density range of 1-8A dm^{-2}. At cell current of 3 A, the Hull cell panels showed burnt deposit at higher current density regions. This observation revealed that the bath gave bright deposit in the current density range 1-8 A dm^{-2} at 2 A cell current in the current density range 1-8 A dm^{-2} as shown in (Figure 1(l))

3.1j Polarization studies

The potential of the steel cathode was measured galvanostatically with respect to saturated calomel electrode (SCE) at different current densities. The variation of potential in the presence of different bath constituents is as shown in (Figure (2)). The shift in cathodic potential towards negative direction was observed in presence of addition agents. This could be attributed to the formation of more stable electrical double layer by the condensation product.

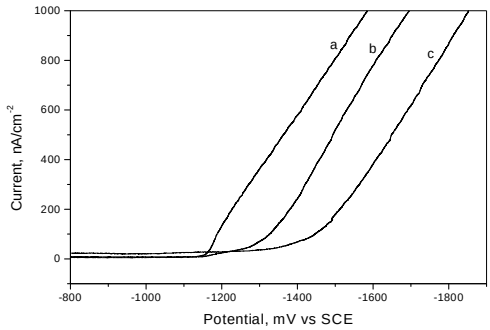


Figure 2 : Effect of addition agents on cathodic potential (a) ZnSO4 +MnSO4 +NaSO4 +H3BO3 (BB) (b) BB+CTAB (c) BB+CTAB+ CP1.

3.1k Current efficiency and throwing power

Current efficiency and throwing power were measured at different current densities by using optimized bath solution. At 1.0 A dm^{-2}, the current efficiency was found to be 70%, and at a current density of 2 A dm^{-2} the current efficiency was found to be 73%. With increase in current density above 4 A dm^{-2}, the current efficiency was found to be decreased.

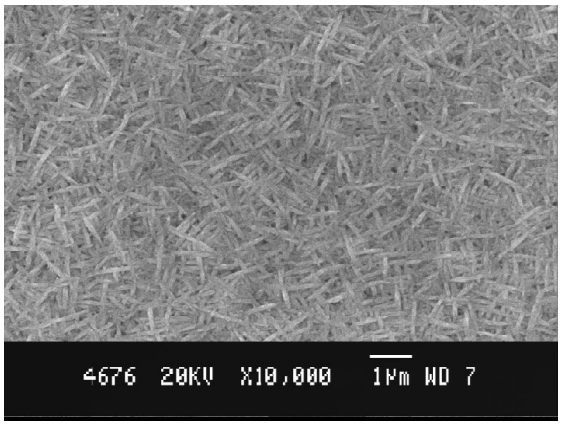
Throwing power was measured by using Haring and Blum cell at different current densities. At low current densities, the throwing power was 18% and with increase in the current densities it was increased to 25%. As shown in (Table (3)).

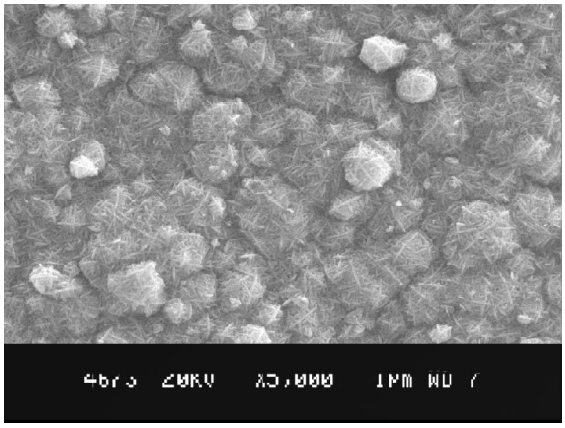
Table 3. Current efficiency and throwing power at different current densities

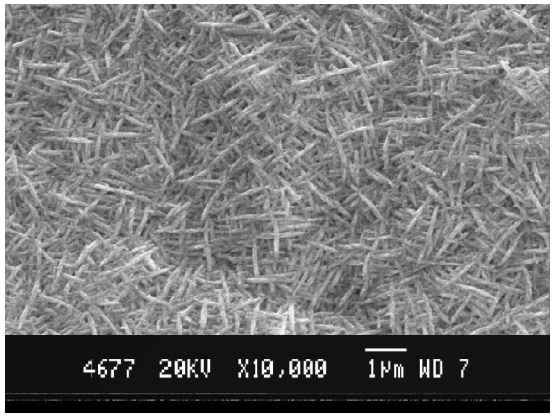
Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1	70	18
2	73	19
3	77	21
4	91	23
5	81	25

3.1l Surface morphology and IR studies

The nature of crystal growth in the presence and absence of addition agents is explained with the help of SEM photomicrographs (JEOL-JSM-35 LF). SEM photomicrograph of the deposit obtained from the basic bath shows coarse grained deposit having irregular crystal size. In presence of CTAB, the grain size is smaller (~40 nm) indicating a modification in the rate of crystal growth. It is also noteworthy to mention that the porous free nature of the coating is due to the smaller grain size. The change in morphology could be attributed to a strong blocking effect of the cationic surfactant which causes an increased nuclei renewal rates leading to an increase in nucleation number and hence smaller grain size. The SEM photomicrograph of the deposit obtained from the optimum bath shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit. The average grain size of the deposit is ~30 nm (Figure (3)).







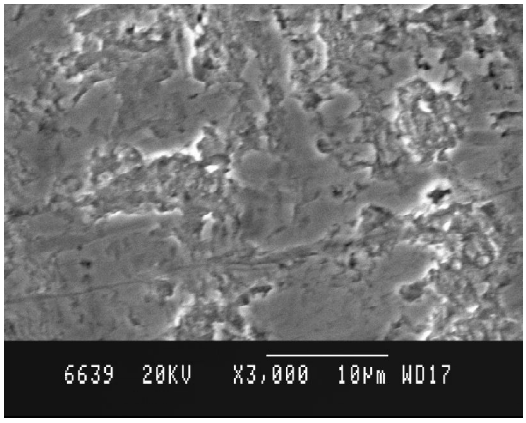


Figure 3 : SEM photomicrographs of the deposits obtained in the presence and absence of addition agents at 298 K ; (a) Basic bath (BB), (b) BB + CTAB, (c) BB + CTAB + CP1, (d) Optimized bath.

The IR spectrum of scraped deposit obtained from the optimum bath was used to test the inclusion of addition agent in the deposit. IR spectrum shows an absorption peak at 1629.6 cm^{-}

[1] which corresponds to >C=N- group of condensation product. This confirmed the inclusion of condensation product in the deposit during electrode position. The molecules of brightner are preperentially $_{adsorbed}$ on the peak of dendritic growth sites on the cathode surface, preventing further growth of their peaks, leading to a smoother surface. (Figure (4)) shows the IR spectrum of the scraped deposit.

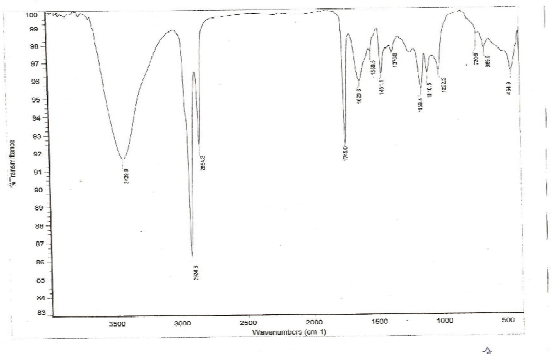


Figure 4 : IR spectrum of scraped Zn-Mn alloy deposit.

3.2 X-ray diffraction studies

The crystal structures of the Zinc coatings with and without additives were investigated by using X-ray diffraction technique. The 2q values of the sample match with the standard JCPDS file. The crystalline size was determined from the full width at half maximum of the X-ray peaks present on the diffract gram and corresponding results are given in table 4 and 5, (Figure (5 & 6)).

Table 4. Parameters derived from XRD data, In deposit from basic bath

Deposit	2*q*	Average crystal size (nm)	'd' spacing	*hkl*
Zn	36.30	32.26	2.4727	(0 0 2)
	39.01	31.26	2.3069	(1 0 0)
	43.24	30.29	2.0905	(1 0 1)
	54.34	29.17	1.6868	(1 0 2)
	70.05	39.26	1.3421	(1 0 3)
	82.07	49.65	1.1732	(1 1 2)
	86.53	51.44	1.1238	(2 0 1)

Table 5. Parameters derived from XRD data. In deposit from optimized bath

Deposit	2θ	Average crystal size (nm)	'd' spacing	*hkl*
Zn-Mn	31.69	26.67	2.8211	(0 0 2)
	36.30	21.28	2.4727	(1 0 0)
	38.97	26.19	2.3092	(1 0 1)
	43.21	24.76	2.0919	(1 0 2)
	54.33	20.29	1.6871	(1 0 3)
	70.13	35.40	1.3407	(1 1 2)
	82.05	17.02	1.3333	(2 0 1)

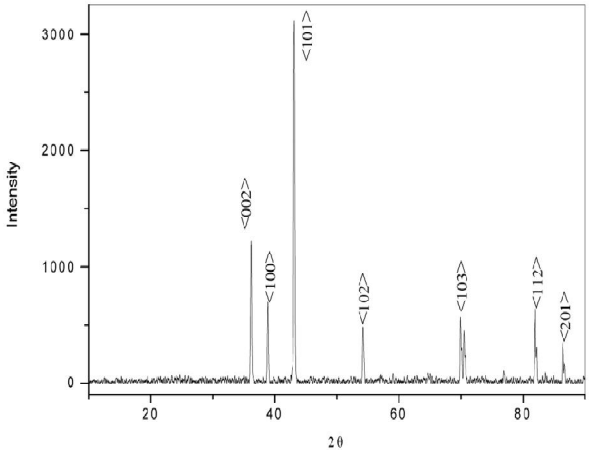


Figure 5 : X-ray diffraction pattern of zinc obtained from basic bath.

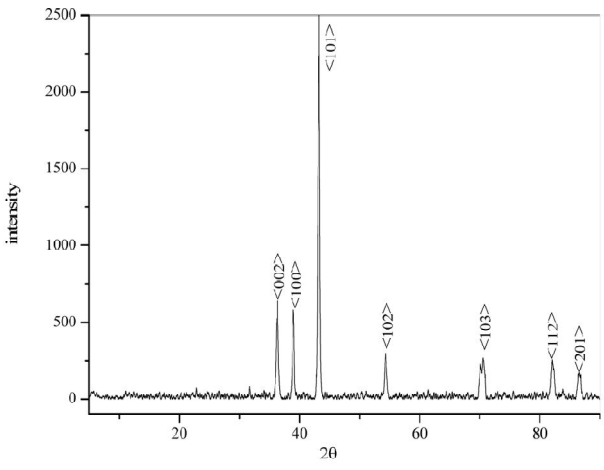


Figure 6 : X-ray diffraction pattern for Zn-Mn alloy obtained from optimum bath.

4. Conclusion

In the present work Zn-Mn alloy deposit has been obtained from sulphate bath at different current densities. The performance of bath solution towards alloy coating was established from the results of polarisation, current efficiency and throwing power. The IR spectrum revealed the inclusion of additive in the deposit. The SEM images indicated that the deposit obtained from the optimum bath has got perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence resulted in the bright deposit. The deposits were analyzed by X-ray diffraction method. The addition agents are non-toxic, easily soluble in water and hence require no treatment the effluent. The bath could be easily scale up to pilot electroplating.

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