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Research Article

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Effect of polyethylene glycol on electrodeposition of nano crystalline zinc

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ABSTRACT

Nano crystalline zinc coatings were deposited from acid bromide bath containing polyethylene glycol. The effect of additives and current density on the deposit nature was investigated through Hull cell experiments. The role of polyethylene glycol on cathode current efficiency, rate of build up and nature of deposit at different temperatures were discussed. Micro hardness of zinc deposits was determined. The surface morphology of the zinc deposits was studied by scanning electron microscopy (SEM). The preferred orientation and average size of the zinc electrodeposits were obtained by X-ray diffraction analysis.

Key words: Nano crystalline zinc, Zinc bromide, Current efficiency, Poly ethylene glycol

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INTRODUCTION

Zinc electrodeposits offer good corrosion resistance to ferrous metal parts at low cost [1]. The combination of aesthetic finish and protection thus provided has established bright zinc plating as an important process in modern industry. The corrosion resistance of zinc electrodeposits may further be improved with a suitable chromate conversion coating. Zinc coatings can be obtained from cyanide, alkaline non-cyanide or acid type of electrolytes. [2-11]. In recent years, nano crystalline zinc coatings have received great research interest because the nano structured materials show considerable changes in mechanical, physical and chemical properties in comparison with conventional poly crystalline materials [12]. Nano crystalline materials may be produced in a number of ways, including gas condensation, spray conversion, ball milling and electrochemical deposition [13-15]. The properties of the deposits depend on a number of factors such as composition and metallurgical structure, which are in turn affected by the deposition conditions. These parameters include current density, electrolyte composition, pH and temperature as well as on the type and the amount of additives included in the electrolyte [16-20].

In the present investigation, the effect of additives during the electrodeposition of zinc from bromide solutions, the role of polyethylene glycol on cathode current efficiency, rate of build up and nature of deposit at different temperatures. Micro hardness of zinc deposits was determined. The surface morphology was investigated by scanning electron microscope and the preferred orientation and average size of the zinc electrodeposits were obtained by X-ray diffraction analysis.

EXPERIMENTAL SECTION

The basic bath containing zinc bromide 160 g/l, boric acid 40g/l and potassium bromide 50 g/l l was used to study the effect of brighteners.

Plating experiments were carried out using polished cold-rolled mild steel specimens subjected to the usual pretreatments like solvent degreasing, alkaline electro cleaning and 5% acid dip. High purity (99.9%) zinc was used as the anode. The optimum current density range for obtaining quality deposits from the selected plating bath was

determined by Hull cell experiment using a standard 267 ml cell [21]. The Hull cell experiments were carried out at 1A cell current for 5 minutes duration at 30° C.

The cathode current efficiency (CCE) and rate of build up at different current densities were determined from the weight of deposit on the cathode of (7.5 x 2.0) cm size, at different temperatures.

Throwing power (TP) was measured in a Haring-Blum [22] cell. A porous zinc anode was placed between two plane parallel steel cathodes filling the rectangular cell cross section. One of the cathodes was nearer to anode than the other. The distance ratio was 5: 1. The percentage of the throwing power was calculated from Field's formula [23].
Micro hardness of electrodeposits of zinc was determined on the Vicker's scale by using LECO Tester. In this method, a diamond pyramid was pressed into the deposit under a load of 25 g for 15 seconds and the indentation diagonal was measured after the load was removed. The micro hardness of the deposit in Kg / mm^2 was determined in each case by using the formula.

$$\text{Vicker's Hardness (kg / mm}^2\text{)} = \frac{1854 \times P}{d^2}$$

where P - the load applied in grams and d - diagonal of the indentation obtained in micrometers

The morphology of the electrodeposits was examined at x 2000 magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope (JEOL-JSM-35 LF). Powder X-ray diffraction (Philips TW 3710) was carried out using nickel-filtered Cu-Kα radiation for determining the lattice parameter, crystallographic texture and approximate grain size of the deposit. The grain sizes of the coating were determined using the Scherrer's equation [24].

RESULTS AND DISCUSSION

The effect of brighteners was studied in the zinc plating bath containing zinc bromide 160 g/l, boric acid 40g/l and potassium bromide 50 g/l l at a cell current of 1A, pH 4 and 30^{o}C and the results are presented in Figs. 1 to 4. Fig.1 presents the legend used for Hull cell studies.

Effect of thio urea
The amount of thio urea in the bath was varied from 0.5 to 2.0 g/l and the results are given in Fig.2. From the figure, it may be seen that thio urea gives grey and matte white deposits.

Effect of polyethylene glycol
Fig.3 presents the deposit pattern obtained with polyethylene glycol (PEG) in the bath under study. When the quantity of polyethylene glycol was 1.0 g/l, a semi bright milky deposit was observed upto1.8 A/dm^2. Grey and matte white deposits were observed beyond this current density. Further increase in the concentration of polyethylene glycol resulted in a decrease in the semi bright milky region. Hence, 1.0 g/l polyethylene glycol was noted as the optimum concentration.

Effect of thiamine hydrochloride
The concentration of thiamine hydrochloride was varied from 0.5 to 2.0 g/l in the bath under study and the results are presented in Fig. 4. From the figure, it may be seen that thiamine hydrochloride gives grey deposit at all concentrations.

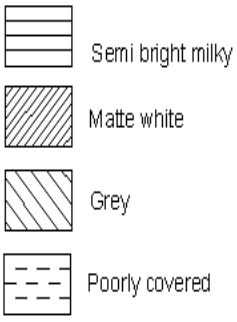

Fig.1: Legends used for Hull cell studies

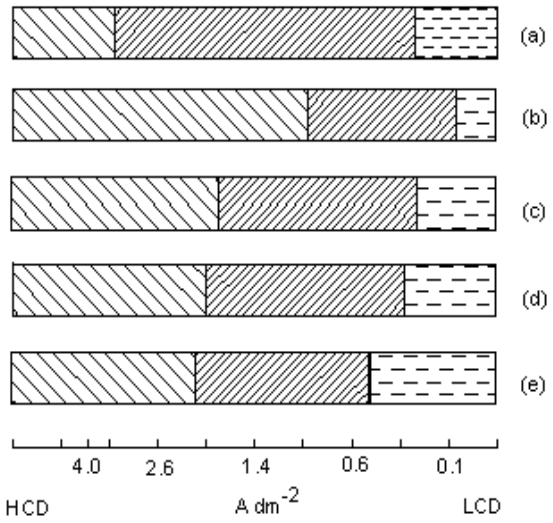

Fig. 2: Effect of change of concentration of Thio urea.

Bath Composition and Conditions: Zinc bromide - 160g/l, Boric acid - 40g/l, Potassium bromide - 50g/l and Thio urea (g/l) (a) 0, (b) 0.5, (c)1.0, (d) 1.5, (e) 2.0, Cell Current - 1A,Temperature - 30° C and pH 4.

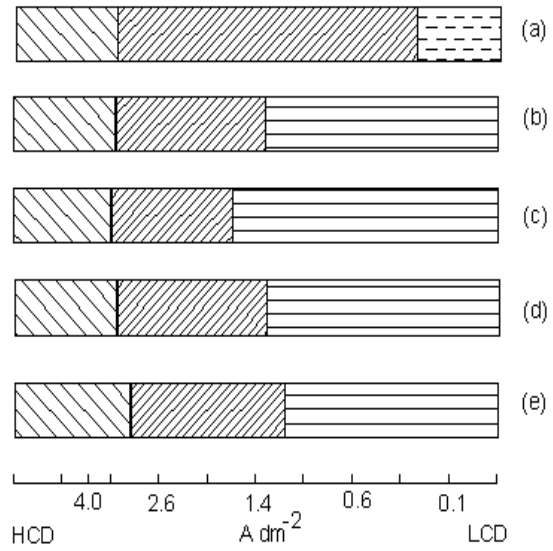

Fig. 3: Effect of change of concentration of Polyethylene glycol.

Bath Composition and Conditions: Zinc bromide - 160g/l, Boric acid - 40g/l, Potassium bromide - 50g/l and Polyethylene glycol (g/l) (a) 0, (b) 0.5, (c)1.0, (d) 1.5, (e) 2.0, Cell Current - 1A,Temperature - 30° C and pH 4.

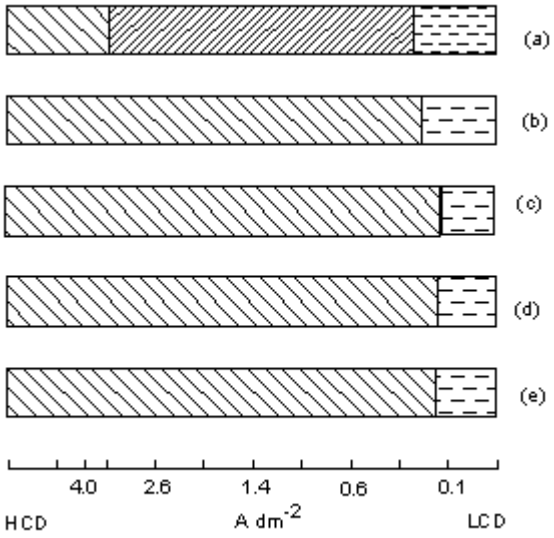

Fig. 4: Effect of change of concentration of Thiamine hydrochloride.

Bath Composition and Conditions: Zinc bromide - 160g/l, Boric acid - 40g/l, Potassium bromide - 50g/l and Thiamine hydrochloride (g/l) (a) 0, (b) 0.5, (c)1.0, (d) 1.5, (e) 2.0, Cell Current - 1A,Temperature - 30° C and pH 4. From this Hull cell studies, it can be noted that the bath containing zinc bromide 160g/l, boric acid 40 g/l, potassium bromide 50 g/l and polyethylene glycol 1.0g/l, operated at pH 4 and at 30^{o}C produced semi bright milky deposit at low current densities.

Cathode Current Efficiency and Throwing Power

Table 1 presents the different bath compositions used in the present investigation. The influence of current density on deposition characteristics at different temperatures under moderate agitation are given in Tables 2 and 3. The results show that the cathode current efficiency increasing with current density up to 2.0 A/dm^2 and then decreases with further increase in current density. This is due to the hydrogen evolution occurring at the cathode along with zinc deposition at the high current densities [5]. The rate of build up increased with current density. Also, it may be seen that the current efficiency decreases with temperature. Matte white deposits were obtained in the absence of polyethylene glycol whereas in the presence of polyethylene glycol, semi bright milky and matte white deposits were obtained.

Throwing power values at different current densities for bath A and bath B are given in Table 4. Throwing power of 13.45% was observed for the bath B at 2.0 A/dm^2. Deposition from complex baths usually takes place at higher cathode potentials and is hence associated with enhanced throwing power [25]. On the other hand non-complexing electrolytes are associated with less throwing power.

Micro hardness

The results of micro hardness of zinc electrodeposits of 35 µm are given in Table 4. The hardness of 73 kg/mm^2 was obtained for the zinc deposit from bath B and 64 kg/mm^2 from bath A at 1.0 A/dm^2. Hardness values obtained at 2 A/dm^2 showed a lesser value irrespective of the bath compared to values for 1 A/dm^2. The deposits were found to be coarse at higher current density and hence a decreased value was obtained.

Table 1: Bath compositions used in the present investigation

Bath	Composition (g/l)	
A	Zinc bromide	160
	Boric acid	40
	Potassium bromide	50
	pH	4
B	Zinc bromide	160
	Boric acid	40
	Potassium bromide	50
	PEG	1.0
	pH	4

Table 2: Deposition characteristics of bath 'A' at different temperatures under moderate agitation

Temp (^oC)	Current Density (A/dm^2)	Current Efficiency (%)	Rate of Build Up (μm/hr)	Nature of the Deposit
30	1.0	98.5	4.21	Matte white
	2.0	99.0	8.46	Matte white
	3.0	94.8	12.16	Matte white
	4.0	91.2	15.60	Matte white
40	1.0	97.3	4.15	Matte white
	2.0	98.1	8.39	Matte white
	3.0	93.0	11.93	Matte white
	4.0	90.5	15.47	Matte white
50	1.0	96.8	4.14	Matte white
	2.0	97.0	8.29	Matte white
	3.0	92.2	11.83	Matte white
	4.0	89.1	15.23	Matte white

Table 3: Deposition characteristics of bath 'B' at different temperatures under moderate agitation

Temp(^oC)	Current Density (A/dm^2)	Current Efficiency (%)	Rate of Buildup (μm/hr)	Nature of the Deposit
30	1.0	96.8	4.13	Semi bright milky
	2.0	97.3	8.32	Semi bright milky
	3.0	93.4	11.98	Matte white
	4.0	90.0	15.39	Matte white
40	1.0	93.5	3.99	Semi bright milky
	2.0	95.4	8.15	Semi bright milky
	3.0	89.7	11.50	Matte white
	4.0	85.0	14.53	Matte white
50	1.0	92.4	3.95	Semi bright milky
	2.0	93.5	7.99	Semi bright milky
	3.0	88.2	11.40	Semi bright milky
	4.0	83.3	14.25	Matte white

Table 4: Throwing power for electrodeposition of zinc baths at 30^{o}C

Bath	Current Density (A/dm^2)	Throwing power (%)
A	1.0	+6.78
	2.0	+7.44
B	1.0	+9.72
	2.0	+13.45

Table 5: Micro hardness of electrodeposits from various baths at 30^{o}C

Bath	Current Density (A/dm^2)	Vicker's micro hardness (kg / mm^2)
A	1.0	62
	2.0	54
B	1.0	73
	2.0	64

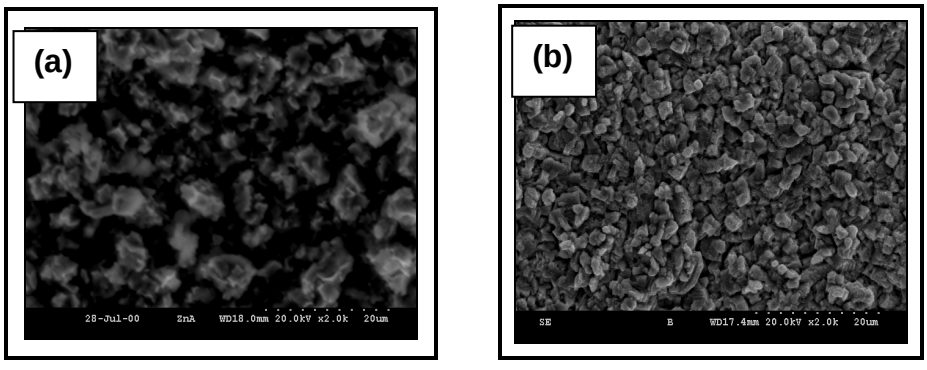

Fig.5: SEM photographs of zinc deposits (a) Deposit A, (b) Deposit B

Surface morphology of zinc deposits

The nature of crystal growth in the presence and absence of addition agents is explained with the help of SEM photomicrographs and is given in Fig. 5. When viewed at 2000 X magnification in the scanning electron microscope, the zinc deposits 'A' exhibited irregular distribution of various crystallites. The surface of the electro

deposit 'B' exhibited regular medium sized crystallites covering the surface completely indicating perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit.

Structure of zinc deposits

Fig. 6 shows X-ray diffraction patterns of the zinc electrodeposits obtained from the zinc bath with PEG. arameters derived from XRD pattern for deposit B are given in Table 6. The observed 'd' value is in good agreement with the standard values for zinc deposition (Joint Committee on Powder Diffraction System/ASTM File No. 1* 40831Zn). Crystalline size was determined from the full width at half maximum (FWHM) of the X-ray peaks using Scherrer's equation. The average size of the deposit was approximately 36 nm.

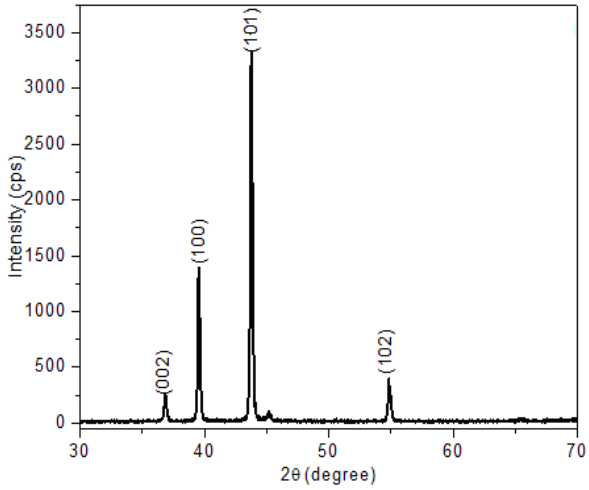

Fig.6: XRD pattern of zinc deposit B

Table 6: Parameters derived from XRD pattern for deposit B

Sl.No	2θ (degree)	d (observed) (A^0)	d (standard) (A^0)	h k l
1	36.88	2.435	2.473	0 0 2
2	38.56	2.287	2.308	1 0 0
3	43.78	2.066	2.091	1 0 1
4	54.84	1.673	1.687	1 0 2

CONCLUSION

From the experiments carried out, the zinc plating bath containing zinc bromide 160 g/l, boric acid 40g/l potassium bromide 50 g/l and polyethylene glycol 1.0 g/l produced semi bright milky, uniform and fine grained deposit and XRD analysis confirmed the formation of nano crystalline zinc deposition.

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