



ROLE OF ADDITIVES ON THE ELECTROCHEMICAL BEHAVIOR OF Cu-Zn ALLOY DEPOSIT FORM ACID TARTARTE BATH

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ABSTRACT

Cu-Zn coatings obtained by electrodeposition from acidic sulphate solutions containing sodium potassium tartate and trisodium citrate as the complexing agents have been studied. The effect current density, pH and temperature on the throwing power of the bath as well as their effect on the alloy composition were monitored. The solution affords good throwing power and current efficiency in presence of the additives under the experimental conditions. Of the different additives tried saccharin and phenol are found to be accelerators while thiourea and glycerine are retarders on the deposition process. Besides, these additives have been examined for their corrosion resistance behaviour with Cu-Zn deposits in 3.5 % NaCl solution medium through Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy Techniques. The subtle role played by the additives in controlling the quality of the deposit has been studied using Scanning Electron Microscope (SEM). The X-ray diffraction analysis revealed that the phase structure of alloy to be an orthorhombic crystal. Based on the above studies, the optimum composition of the bath and the controlling variables for the Cu-Zn deposition are predicted.

Keywords: Cu-Zn alloys, Tafel polarization, X-ray diffraction, SEM, EIS

1. INTRODUCTION

Cu-Zn alloy deposits are widely used for decorative purposes [1, 2], although only the toxic cyanide bath has been used for commercial brass plating purposes. Among a number of non-cyanide pyrophosphate baths appears to be one of the most promising alternatives to the commercial cyanide bath [2-4]. The most widely used plate is yellow brass, which contains 70-pct copper and 30-pct zinc [5]. The important aspects of brass plating are the ratio of copper to zinc and the level of free cyanide. The former should be maintained between 2.3:1 and 2.6:1 with 2.3:1 being ideal; the latter should be at a level equal to zinc metal. Alloys with more than 80 pct copper are red in color and include the commonly used 85/15 and 80/20 alloys. They are called red brass finishes. The substitution of tin for zinc will produce an alloy with a color close to that of gold and is frequently used in the architectural trades. The very desirable yellow-green brass is controlled by grain size. The slight green cast is developed with grain refiners. The Copper-Zinc alloy coatings are deposited on mild steel substrates using pyrophosphate-based electrolyte at room temperatures and under continuous current [6, 7].

The present study involves the determination of cathode current efficiency, throwing power, and determination of optimum composition of deposit for the acid tartrate bath containing different additives. The electrodeposition studies described here are designed to evaluate the effect of some additives on the properties of Cu-Zn deposits from an acid tartrate bath. The structure and surface morphology of the alloy deposits were studied.

2. EXPERIMENTAL DETAILS

All the experiments were carried out with fresh solutions using double distilled water and high quality pure chemicals. The bath composition specified later was used at room temperature. The cathode current efficiency measurements were carried out in a cell consisting of two electrodes and a regulated power supply. The stainless steel substrates and titanium metal were used as cathode and anode respectively. Electrodeposition was carried out at specific current densities for specific time durations. The deposits were dried and weighed to calculate the cathodic current efficiency. The Cu-Zn alloy was deposited onto stainless steel cathode and the deposit was dissolved in a solution of 1:1 HNO_3 . The composition was determined using atomic absorption spectroscopy.

Electrochemical impedance spectroscopy measurements and potentiodynamic polarization studies were carried out in 3.5 % NaCl medium to evaluate the corrosion protection behavior of these deposits. A three-electrode polarization cell assembly was used to carry out the experiment. The deposit of 1cm^2 area was used as the working electrode. The Pt foil was used as counter electrode and SCE as the reference electrode. The deposits were immersed in NaCl solution for 5-10 minutes time intervals to allow for the system to attain the steady state equilibrium. The experiments were carried out at the corrosion potentials in the frequency range of 10 KHz to 100mHz with superimposed AC voltage of amplitude 10 mV using EG&G impedance analyzer, Model 6310. The same cell setup was adopted for potentiodynamic polarization studies also.

3. RESULTS AND DISCUSSION

3.1 Hull cell studies

Electroplating experiments were carried out, in order to study the effect of plating variables Viz., metal ion ratio in the bath, current density (cd), pH, temperature, Stirring and concentrations of the complexing agents. Using the Hull cell experiments the current density was optimized. Control of pH and temperature of the plating bath is necessary to attain optimum efficiency and maintain the desired physical properties of the deposits. Hence, electroplating was carried out at different pH values 4 - 8 and at temperatures 30 - 70°C and at different current densities 0.2 - 0.7 A/dm^2 . The results are given in the Table 1. Uniform, bright and mirror yellowish brass deposits were obtained with a current density of 0.5 A/dm^2 . The optimum pH to get mirror bright and good adherent deposit was found to be 4. In the alkaline conditions, the deposit appearance seemed to be of black and pinkish in colour.

Uniform and bright yellow brass deposits were obtained at the temperature of 30°C and at higher temperatures only black deposits were obtained. The optimum temperature to get adherent quality deposit was found to be 30°C. Comparatively smooth and fine-grained coatings were produced by adding any of the surfactants (saccharin, thiourea, glycerine and phenol) to the electrolytic bath. The exact physical appearance of the deposits caused by these additives are presented in the Table 2. It can be seen that the addition of saccharin, thiourea, glycerine and phenol favors the formation of bright yellow and black deposits. Bright Brass deposits were obtained with the addition of 0.005 to 0.04 gpl of phenol. It is mentioned that there are number of reports [8-10] on this aspect. A mirror bright brass deposit was obtained with the addition of 0.002gpl of phenol in the bath solution. However with high concentration of phenol only blackish deposit was obtained.

The throwing power, current efficiency and alloy composition are varied with current densities. The results are shown in Table 3. The throwing power decreases with increase in the current density for the plating process. Any increase in the current density above 0.5 A/dm^2 results in appreciable loss of the throwing power. As a result, a bright and adherent deposit could obtain at current densities below 0.5 A/dm^2 .

The current efficiency decreases with increase in the current density due to wastage of current with some of the unwanted side reactions like discharge of proton that are encountered during the plating process. When the current density increases in the bath, the percentage of copper content increases in the deposit. Hence higher current densities favor copper rich deposits.

The effect of temperature and pH on the composition of the yellow brass deposit is given in Table 4. At higher temperature the deposit has higher copper content. This could be due to either enhanced preferential mass transport of copper or due to decreased copper over potentials compared with those of Zn case in the bath. It is seen from the table that copper becomes rich at the expense of Zn in the deposits.

The effect of addition agents on the throwing power and current efficiency for the deposition process are shown in Table 5 for an optimum concentration. Using an optimum concentration of the addition agents could enhance the throwing power and current efficiency.

The results for the influence of the addition agents on the rate of deposition are presented in Table 6. Some organic compounds added to the solution strongly affect the alloy plating process [11]. The rate of deposition increases with increase in the concentration of the addition agents. The addition of thiourea for bright deposits was reported [12, 13]. An optimum concentration of 0.02 gpl of thiourea has been recommended to get bright deposit. At higher concentration (0.03gpl) the rate of deposition was slightly decreased. The same results were obtained with the addition of glycerine.

Coats [14] has reported that 3gpl of Phenol to increase the Zinc content by over 3 % in the deposit. In the present study it is found that the rate of deposition is increased with the increase in the concentration level of phenol upto 0.04 gpl. A bright yellowish deposit was obtained when the concentration was in the lower level of 0.005 gpl in the plating bath. In the case of saccharin also the rate of deposition increases with the increase in the concentration in the ranges 0.002-0.15 gpl.

3.2 Corrosion Studies

3.2.1 Potentiodynamic polarization Studies

The potentiodynamic polarization curve for the Cu-Zn alloys obtained with and without additives in the plating bath in 3.5 % NaCl electrolyte are presented in Figure 1. The E_{corr} and i_{corr} values calculated using the Tafel extrapolation method is given in Table 7. For an effective comparison the corrosion data of mild steel are also included in the same table. There is an appreciable increase in the corrosion resistance for the deposits compared to mild steel. The E_{corr} and i_{corr} values show a positive shift as compared to the base metal in the plain bath indicating enhanced anodic control of the corrosion process.

The better corrosion resistance nature of Cu-Zn deposit obtained from thiourea, a saccharin, glycerine and phenol additive in the bath is due to the fine-grained structure of the deposits obtained in their presence.

3.2.2 Impedance

Table 8 and Figure 2 give the impedance results for the corrosion of electro deposited Cu-Zn deposit on mild steel immersed in 3.5% NaCl. The increase R_t values and decreases in C_{dl} values for the all the deposits clearly confirm the better corrosion resistance of the deposits compared to the bare mild steel substrate in the medium.

3.3 SEM

The morphological features are shown in Figure 3 (a, b, c, d and e) and correlated with the results discussed earlier. Figure 3a shows that irregular and coarse coatings are produced in the base tartarte bath. Interesting results were also obtained with the solutions containing saccharin, glycerine and thiourea (Figure 3b, 3d and 3e). They present regular and refined topography, with small grains and without cracks. The deposits produced in solutions with additions of phenol (Figure 3c) have an irregular, large and coarse-grained structure.

3.4 XRD

The feasibility of co-deposition of various places in Cu-Zn is cited in literature [15]. The X-ray diffraction patterns of Cu-Zn surface are shown in Figure 4. The surface layer compacted is composed of four phases, i.e., Cu-Zn (β -phases, b.c.c), Cu (f.c.c), Cu-Zn (α -phases), and slight amount of ZnO.

4. CONCLUSIONS

Brass plating has been attempted by optimizing the plating conditions. The main conclusions drawn from the present studies are listed below

1. An optimized non-cyanide brass-plating bath different from conventional baths that can give deposits of good quality on mild steel substrates is outlined below.

Copper sulphate	2.5gpl
Zinc sulphate	1gpl
Tri sodium citrate	5gpl
Sodium potassium tartarte	9gpl
pH	3
Temperature	30°C
Time	Half an hour
2. The bath can be operated with 90% efficiency at low current densities in the range 0.3A/dm²
3. The Zinc and Copper contents of the bath decide the composition of the deposit.
4. The deposits obtained at 5 μ /hr rate are found to be pore free and have good adhesion on the steel substrate.
5. The properties of the coatings can be improved by using some additives such as thiourea and saccharin besides obtaining the deposition at appreciable plating rates.
6. Mild addition of phenol to the plating bath is noted to be useful as a brightener.
7. The potentiodynamic polarization studies and impedance measurements confirm the better corrosion resistance of the Cu-Zn deposits.

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TABLES

Table 1: The effect of current density, pH and temperature on the Nature of the deposits

Current Density (A/dm²)	Nature of the deposit
0.3	Bright and pink colour deposit
0.4	Bright yellow pink colour and blacky deposit
0.5	Mirror yellowish and Bright yellowish deposit
0.6	Semi bright and pink deposit
0.7	Pink and black deposit
pH	Nature of the deposit
2	Pink and black deposit
4	Bright yellow and mirror yellowish deposit
6	Yellow and pink and black deposit
8	Pink and black deposit
Temperature (°C)	Nature of the deposit
30	Maximum Bright yellow and yellowish deposits
40	Yellow, pink and black deposit
50	Semi yellow, pink and black deposit
60	Dull yellow, pink and black deposit
70	Pink and black deposit

Table 2: The effect of concentration of addition agents on the Nature of the deposits

Addition Agents	Concentration of Additives	Nature of the deposits
Saccharin	0.002	Semi bright and yellow deposit
	0.004	Bright and yellow deposit
	0.005	Mirror bright yellowish and yellow deposit
	0.01	Bright yellow and pink colour deposit
	0.15	Yellow and blacky deposit
Thiourea	0.001	Yellow and black deposit
	0.005	Bright yellow and black deposit
	0.008	Maximum bright yellowish and yellow deposit
	0.01	Bright yellow deposit
	0.02	Yellow and blacky deposit
Glycerine	0.002	Yellow and black deposit
	0.004	Maximum bright yellowish and yellow deposit
	0.005	Bright yellow deposit
	0.01	Yellow and blacky deposit
Phenol	0.002	Mirror bright yellowish and yellow deposit deposit
	0.005	Bright and yellow deposit
	0.008	Semi bright and yellow
	0.02	yellow and pink colour deposit
	0.04	Yellow and blacky deposit

Table 3: The effect of throwing power, current efficiency and alloy composition at various current densities

Current densities (A/dm ²)	Throwing Power (%)	Current Efficiency (%)	Alloy Composition (%)	
			Cu	Zn
0.3	86	90	58	42
0.4	78	85	68	32
0.5	76	80	64	36
0.6	70	73	76	24
0.7	72	71	78	22

Table 4: The effect temperature and pH on the alloy composition at various current densities

Temperature (°C)	Alloy Composition (%)		pH	Alloy Composition (%)	
	Cu	Zn		Cu	Zn
30	63	37	2	59	41
40	68	32	4	64	36
50	75	25	6	70	30
60	80	20	8	76	24
70	89	11			

Table 5: The effect of addition agents on current efficiency and throwing power of the deposit

Addition agents	Best concentration of additive (gpl)	Current Efficiency (%)	Throwing Power (%)
Saccharin	0.005	95.5	89.4
Phenol	0.002		88.4
Thiourea	0.008	94.6	87.8
Glycerine	0.006	90.5	87.3
		90.0	

Table 6: The effect of addition agents on the rate of deposition

Addition Agents (gpl)	Concentration of Additives	Rate of Deposition (μ/hr)
Saccharin	0.002	2.2
	0.004	3.1
	0.005	4.6
	0.01	4.8
	0.15	5.0
Phenol	0.002	1.8
	0.005	2.5
	0.008	2.8
	0.02	3.9
	0.04	4.5
Thiourea	0.001	2.0
	0.005	2.5
	0.008	2.8
	0.01	3.5
	0.02	3.0
Glycerine	0.002	2.4
	0.004	2.8
	0.005	3.2
	0.01	3.8
	0.15	3.3

Table 7: Evaluation of corrosion resistance in 3.5 % NaCl solution by Potentiodynamic Polarization Studies

Deposit	$-E_{\text{corr}}$ (mV/SCE)	i_{corr} (A/dm^2)
Mild Steel	801.8	1.359×10^{-4}
Cu-Zn	611.2	5.012×10^{-5}
Cu-Zn (Saccharin)	774.9	5.012×10^{-6}
Cu-Zn (Thiourea)	408.8	1.778×10^{-5}
Cu-Zn (Phenol)	366.01	1.413×10^{-5}
Cu-Zn (Glycerine)	715.4	3.21×10^{-4}

Table 8: Evaluation of corrosion resistance in 3.5 % NaCl solution by Impedance studies

Deposit	R_t (ohmcm^2)	C_{dl} (F/cm^2)
Cu-Zn	143.775	11
Cu-Zn (Glycerine)	829.4	221
Cu-Zn (Saccharin)	1012.55	9.9
Cu-Zn (Thiourea)	1006.432	10
Cu-Zn (Phenol)	2319.52	100

FIGURES

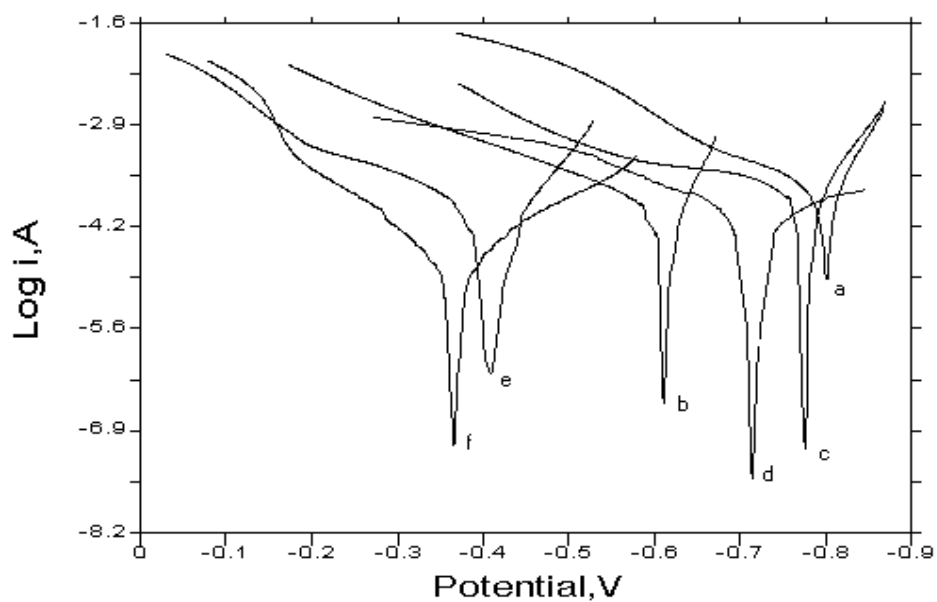


Figure: 1 Potentiodynamic Polarisation Curves of Cu-Zn (With and without additives) in 3.5 % NaCl at 32°C Mild Steel, b) Cu-Zn, c) Cu-Zn (Saccharin), d) Cu-Zn (Glycerine) e) Cu-Zn (Thiourea), f) Cu-Zn (Phenol)

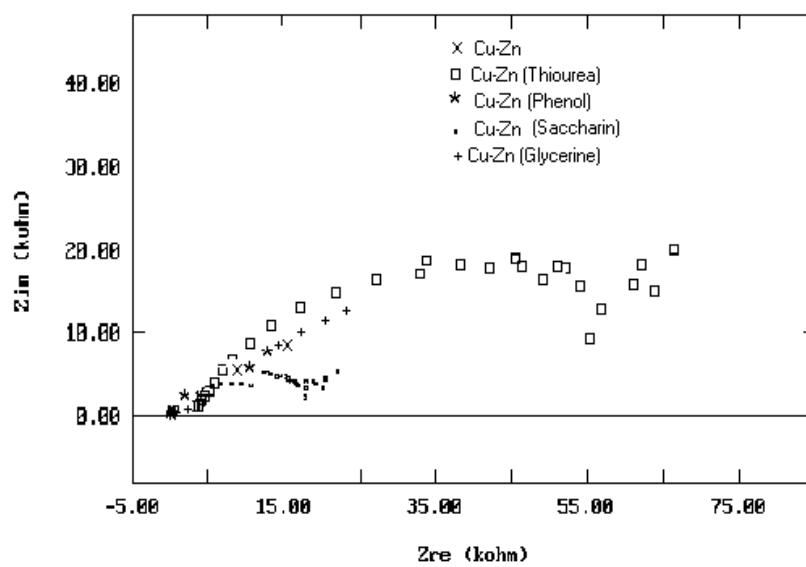


Figure: 2 Impedance curves of Cu-Zn (With and without) additives in 3.5 % NaCl at 32°C

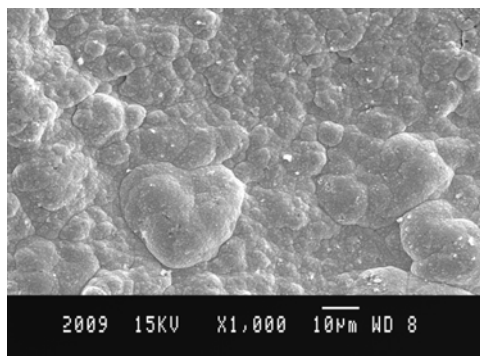


Figure: 3a SEM Photographs of Cu-Zn alloy

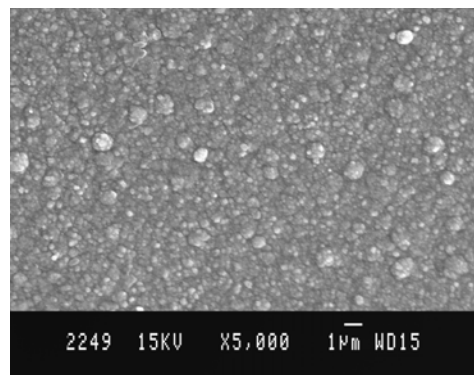


Figure: 3b SEM Photographs of Cu-Zn (Saccharin) alloy

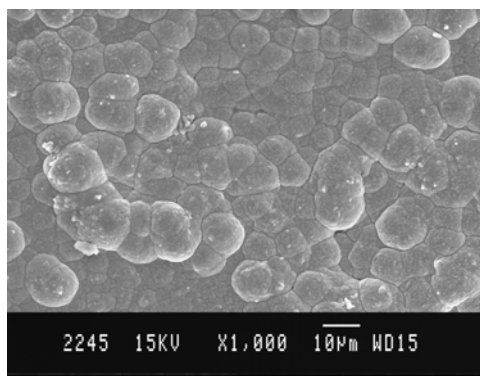


Figure: 3c SEM Photographs of Cu-Zn phenol alloy deposits

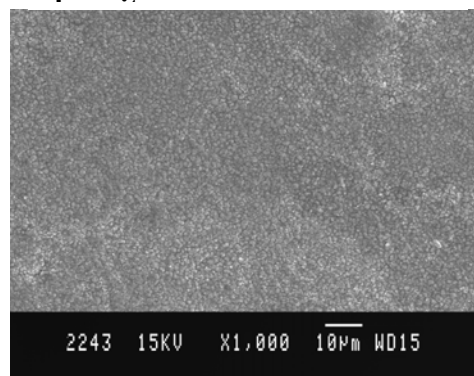


Figure: 3d SEM Photographs of Cu-Zn (glycerine) alloy

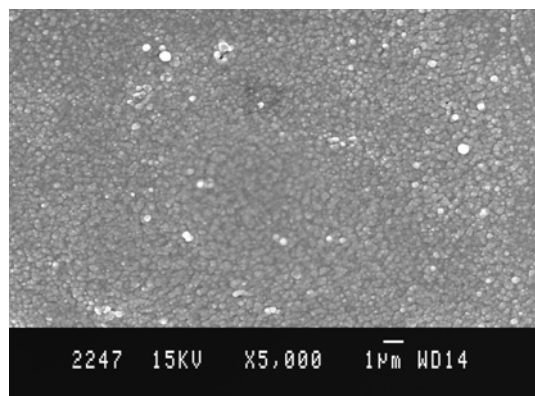


Figure: 3e SEM Photographs of Cu-Zn (thiourea) alloy deposits

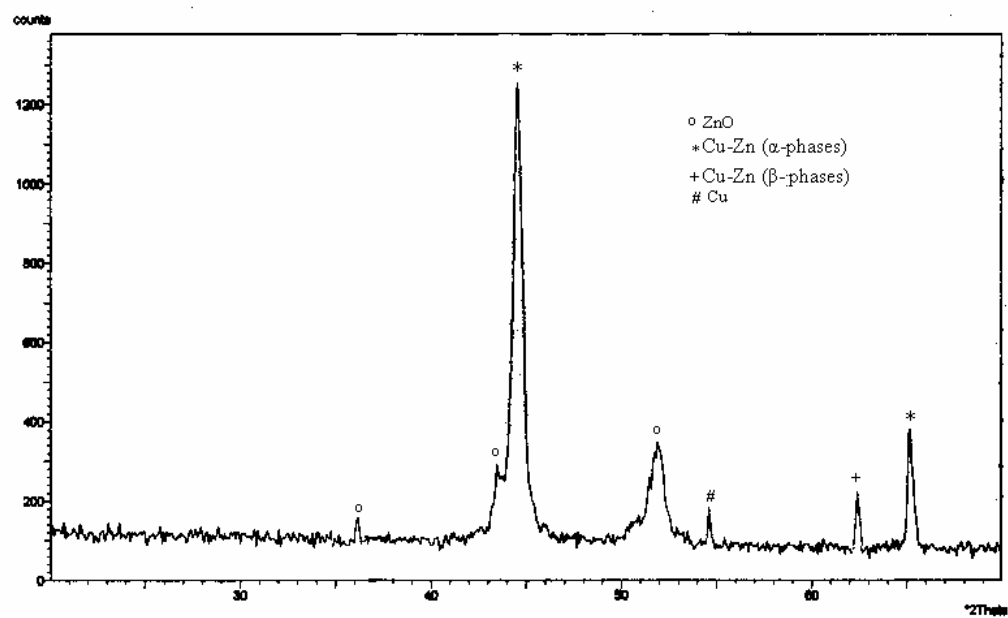


Figure 4: XRD Patterns of Cu-Zn alloy deposit