

Corrosion Resistance of Copper Deposits Produced from Different Electrolytes

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SUMMARY – Plating of steel components with copper prior to nickel and chromium plating is of commercial importance. Copper is used as a pre-plate for improved adhesion of the subsequent deposit. It is also employed to prevent case hardening on selected areas of ferrous metal surfaces. Attempts have been made to carry out copper deposition from a sulphamate electrolyte using an optimised bath composition and operating conditions. Alkaline EDTA, conventional cyanide and acid-sulphate baths have also been used for comparative studies. In the present work the corrosion resistance of copper deposits from these electrolytes has been studied using potentiostatic polarisation techniques, A.C. Impedance spectroscopy and weight loss measurements. Although the deposits from different baths indicate good corrosion resistance, the sulphamate bath gives the most highly corrosion resistant and low porosity deposit.

INTRODUCTION

In decorative copper-nickel-chromium plating, copper deposition helps in improving the corrosion resistance and appearance of the artefact. Automobile bumpers have been plated with 28 μm of copper from an acid-sulphate bath prior to nickel plating^{1,2}. Copper is also used as a pre-plate for improved adhesion of subsequent layers. Deposits from sulphamate baths are similar to those from sulphate baths but are useful for high current density plating of wire, bearings and printing cylinders for the printing industry³⁻⁶. The corrosion resistance of copper deposits obtained from copper-nitrilotriacetate⁷ is comparable with that from conventional acid-sulphate and cyanide baths. The present work provides a comparative evaluation of the corrosion resistance of copper deposits obtained from baths containing sulphamate, EDTA, cyanide and acid-sulphate.

EXPERIMENTAL

Plating Baths

The optimised bath composition and its operating conditions for the production of high quality, adherent copper deposits are:

Sulphamate Bath

copper as $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	32 g dm ⁻³
sulphamic acid	94 g dm ⁻³
dextrin	3 g dm ⁻³
saccharin	1 g dm ⁻³
pH	9.0
Temperature	30° C
Current density	3.0 A dm ⁻²

EDTA Bath

copper as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	32 g dm ⁻³
EDTA- di-sodium salt	60 g dm ⁻³
dextrin	5 g dm ⁻³
saccharin	1 g dm ⁻³
pH	10.5
Temperature	30° C
current density	1.0 A dm ⁻²

Cyanide Bath

copper as CuCN	22 g dm ⁻³
total cyanide	34 g dm ⁻³
sodium carbonate	15 g dm ⁻³
pH	12.0
Temperature	30° C
current density	1.0 A dm ⁻²

Acid-copper Sulphate Bath

copper as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	200 g dm ⁻³
sulphuric acid	100 g dm ⁻³
pH	1.76
Temperature	30° C
current density	1.0 A dm ⁻²

Corrosion Resistance Studies

The corrosion resistance of samples of copper deposited from various copper plating baths was measured using potentiodynamic polarisation techniques, A.C. Impedance spectroscopy and corrosion monitoring via weight loss measurements.

Potentiodynamic polarisation

Corrosion resistance measurements were performed using a three-electrode assembly. The electrodeposited copper specimens were masked with lacquer to expose an area of 1 cm² on one side of the working electrode. A platinum foil and saturated calomel electrode were employed as auxiliary and reference electrodes respectively. Polarisation studies to test the copper electrodeposited from the different electrolytes were carried out in 5% w/v neutral sodium chloride solutions. A constant current generator, fabricated at CECRI, Karaikudi, India, served as the constant current source and a digital voltmeter was used to measure current. The potentials of the electroplated specimens were measured using a digital voltmeter. Steady potentials were observed for the various currents applied.

Potentiodynamic polarisation experiments were carried out using a Wenking potentiostat, and an EG&G (Princeton Applied Research Model 173) potentiostat/waveform generator.

The potentials were scanned at a rate of 20 mV per minute allowing steady state currents to be observed.

AC Impedance Spectroscopy

The same three-electrode cell assembly, as used for the potentiodynamic polarisation experiments, was employed for the AC Impedance investigations. Measurements on copper deposits were carried out in 5% w/v NaCl at open circuit potential using an EG&G Model 6310 frequency response analyser. Impedance measurements were made at open circuit potential applying an A.C. signal of 10 mV in the frequency range 10 kHz to 1 MHz. The values of solution resistance (R_s) and charge transfer resistance (R_{ct}) were obtained from Nyquist plots of the real (Z') vs. imaginary (Z'') components of the impedance. The extent of the corrosion resistance of the coating was assessed from the R_{ct} value, using the Stern-Geary expression shown in equation (1),

$$j_{cor} = \frac{b_a b_c}{2.3(b_a + b_c)} \frac{1}{RT} \tag{1}$$

where b_a and b_c are the Tafel slopes.

Corrosion Monitoring by Weight-loss Measurements

The corrosion rates can be expressed as the variation in the weight per unit surface area and unit time or the penetration of the corrosion process into the metallic material in unit time. In the present study of the corrosion of copper anodes, samples with an area of 5 cm² were immersed in the plating baths for different time intervals. The initial weight of the copper anode was obtained, the sample then placed in the test solution for periods of 30, 60 and 240 minutes, after which time, the sample was removed from the solution, rinsed with distilled water dried and reweighed. The difference in weight gave a measure of the corrosion of the anode in the different plating solutions.

RESULTS AND DISCUSSION

Potentiodynamic Polarisation Studies

Typical polarisation curves obtained for the corrosion behaviour of the plated samples are shown in Figure 1. The data for the samples from the sulphamate bath, Figures 1 (a) – (e) refer to a range of thicknesses from 5.0 to 15.0 μm . Figure 2 shows the polarisation behaviour of a 15 μm thick copper deposit obtained from an EDTA bath, and Figures 3 and 4 that of the same thicknesses of deposit but from cyanide and acid-sulphate baths respectively. Figures 5 and 6 show the polarisation behaviour of mild steel and copper for comparison purposes. Table I includes the values of the corrosion potential (E_{cor}), the corrosion current density (j_{cor}), and the anodic and cathodic Tafel slopes during polarisation in 5% w/v NaCl. The observed positive shift in E_{cor} for the different thicknesses of copper deposits from the sulphamate bath, is indicative of an increasing corrosion resistance with deposit thickness. The observed decrease in j_{cor} for the thicker coatings confirms the improved corrosion resistant behaviour of the

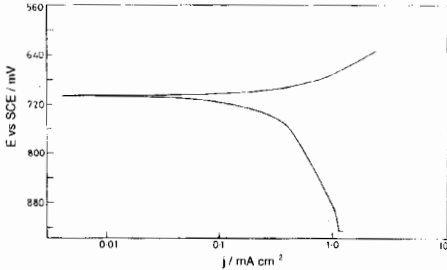


Figure 1. (a) Polarisation studies of copper deposit from sulphamate bath in 5% NaCl (5 μm).

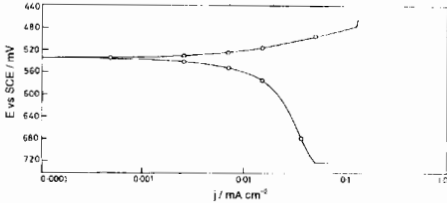


Figure 1. (b) Polarisation studies of copper deposit from sulphamate bath in 5% NaCl (7.5 μm).

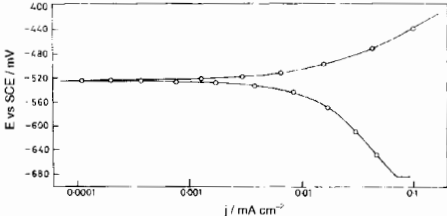


Figure 1. (c) Polarisation studies of copper deposit from sulphamate bath in 5% NaCl (10 μm).

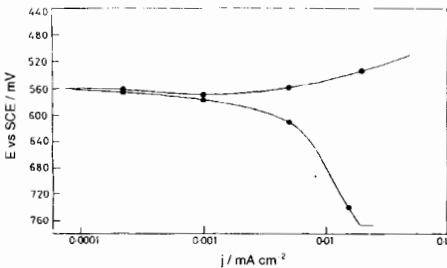


Figure 1. (d) Polarisation studies of copper deposit from sulphamate bath in 5% NaCl (13 μm).

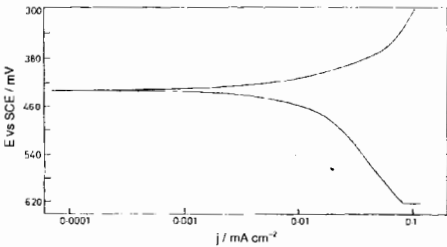


Figure 1. (e) Polarisation studies of copper deposit from sulphamate bath in 5% NaCl (15 μm).

copper. This will also be due to a reduction in porosity at increased coating thicknesses. In the case of the coating produced from the EDTA bath, the E_{cor} value shifts to a more negative value suggesting a reduction in the corrosion resistant nature of this coating compared to that obtained from the sulphamate bath for thickness 15 μm . The copper deposited from the cyanide electrolyte

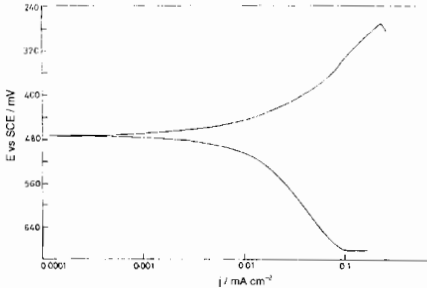


Figure 2. Polarisation studies of copper deposit from EDTA bath in 5% NaCl (5 μm).

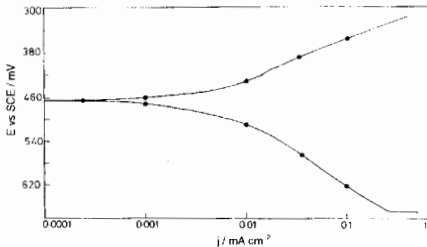


Figure 3. Polarisation studies of copper deposit from cyanide bath in 5% NaCl (15 μm).

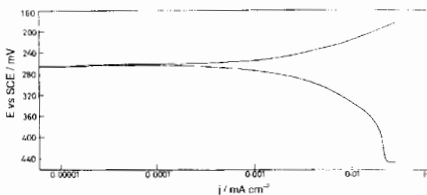


Figure 4. Polarisation studies of copper deposit from acid bath in 5% NaCl (15 μm).

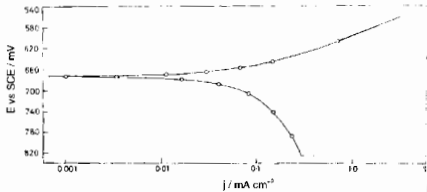


Figure 5. Polarisation studies of pure mild steel 5% NaCl.

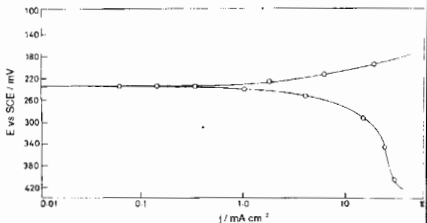


Figure 6. Polarisation studies of pure copper 5% NaCl.

shows an intermediate level of corrosion resistance. The measured values of j_{cor} support these observations. The anodic Tafel slopes of 40 and 70 mV decade⁻¹, for the sulphamate and EDTA/cyanide baths respectively support the corrosion resistant trends for the coatings. The cathodic Tafel slopes of <140 mV decade⁻¹, are also indicative of the corrosion resistant nature of the deposits. O

Table I. Corrosion Parameters of Copper Samples Deposited from Different Copper Plating Baths

S. Plating Baths No.	Thickness / μm	E_{corr} vs SCE / mV	Tafel slope		j_{corr} cathodic / $\mu\text{A cm}^{-2}$	Corrosion rate / mpy
			b_a / mV decade ⁻¹	b_c / mV decade ⁻¹		
1. sulphamate copper bath	5.0	-715	40	-110	25.0	32.20
2. -do-	7.5	-533	40	-135	10.0	12.88
3. -do-	10.0	-525	45	-90	6.8	8.75
4. -do-	13.0	-560	35	-90	6.6	850
5. -do-	15.0	-431	40	-135	2.5	3.20
6. EDTA copper bath	15.0	-473	70	-90	5.5	7.08
7. Cyanide copper bath	15.0	-465	70	-90	3.5	4.50
8. Acid-copper bath (on brass)	15.0	-265	60	-100	2.0	2.57

these, the values for the 15 μm thick coating produced from the sulphamate bath suggest that it should possess the best corrosion resistance performance.

Since the E_{corr} values follow the order,

sulphamate>cyanide>EDTA

and the trend in j_{corr} is,

sulphamate<cyanide<EDTA

the corrosion resistant nature of the deposit should be,

sulphamate>cyanide>EDTA.

In the case of the acid-sulphate bath, the copper was deposited onto a brass substrate and so its corrosion resistance cannot be used for comparison.

A.C. Impedance Spectroscopy Studies of Copper Deposits

The corrosion behaviour of copper-coated samples in 5% w/v NaCl was evaluated by A.C. Impedance measurements. The results are shown in Figures 7-10 and the corresponding corrosion data in Table II. Figures 7 and 8 show Nyquist plots of 15 μm thick copper deposits obtained from the sulphamate and EDTA baths. Similarly, Figures 9 and 10 present Nyquist plots of the same thickness of deposit from cyanide and acid-sulphate baths (at room temperature). Table II gives the values of OCP, charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) for the copper deposits from the three different baths. In the case of the sulphamate bath, as the OCP is the most positive, this suggests that the deposit should be the most resistant to corrosion. The measured charge transfer resistance of this sample was the highest at 660 Ω , consequently the double layer capacitance would be at a minimum for this deposit. The OCP value tends towards the more noble direction in the following order,

sulphamate> cyanide>EDTA

and the charge transfer resistance values are,

sulphamate>cyanide>EDTA.

The double layer capacitance values (in Ω^{-1}) also follow the order,

sulphamate< cyanide<EDTA

Table II. Corrosion parameters of copper deposited samples (impedance measurements)
Thickness = 15 μm

S.No.	Plating baths	OCP vsSCE / mV	R_{ct} / Ω	C_{dl} Ω^{-1}
1.	Sulphamate	-283	660	0.00028
2.	EDTA	-482	63.86	0.010
3.	Cyanide	-527	132	0.005
4.	Acid	-238	317	0.0008

Table III. Corrosion of copper anodes in different plating electrolytes

Sl.No.	Bath	Weight loss / mg cm^{-2} Duration / min		
		30	60	240
1.	Sulphamate bath	2	10	15
2.	EDTA	10	25	35
3.	Cyanide bath	3	15	21
4.	Acid-sulphate	1	5	9

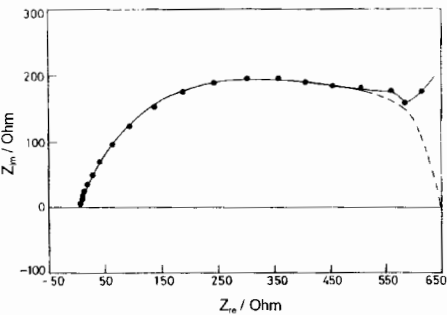


Figure 7. Nyquist plot for corrosion of electrodeposited copper obtained from sulphamate bath (15 μm).

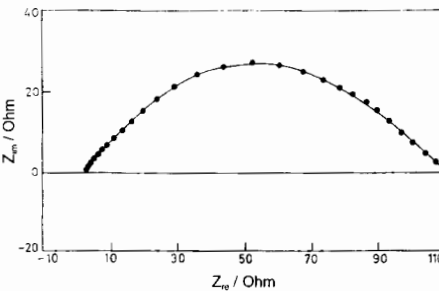


Figure 9. Nyquist plot for corrosion of electrodeposited copper obtained from cyanide bath (15 μm).

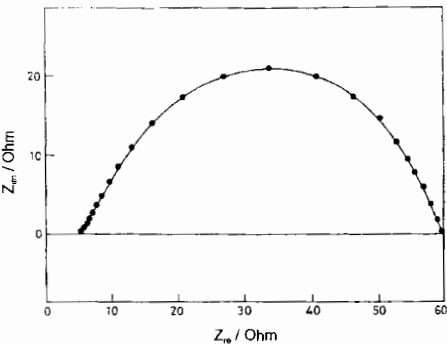


Figure 8. Nyquist plot for corrosion of electrodeposited copper obtained from EDTA bath (15 μm).

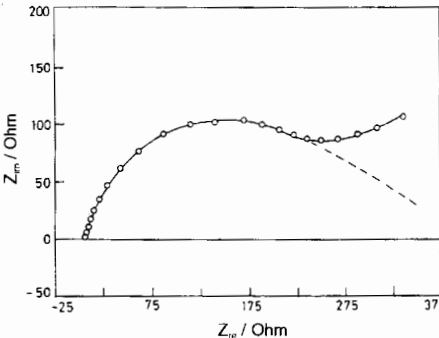


Figure 10. Nyquist plot for corrosion of electrodeposited copper obtained from acid-sulphate bath (15 μm).

thus, the corrosion resistant nature of the deposit will be

sulphamate> cyanide>EDTA.

Since copper is deposited on brass in the acid-sulphate bath, its corrosion parameters cannot be used in a direct comparison but the OCP, R_{ct} and R_{dl} values indicate the high corrosion resistance of the deposit.

Corrosion of the Copper Anodes

Data concerning the corrosion of the copper anodes in the various copper electrolytes at 30°C are shown in Table III. From this, it can be seen that the weight losses observed increase with time irrespective of the electrolyte used. However, the weight loss was greater for the EDTA based copper bath and the lowest for the acid-sulphate bath. The low dissolution in acid-sulphate may be due to passivation of the anode in sulphuric acid in the sulphate bath. In other cases, the complex formation may accelerate anode dissolution allowing the above trends to be observed. The order of dissolution for 240 minutes exposure of copper deposits to the various electrolytes is,

acid-sulphate<sulphamate<cyanide<EDTA.

The corrosion resistance is important when considering application of copper electrodeposits. The coating will only protect the underlying substrate if it is continuous. Where defective, the corrosion rate will depend on the reactivity of the couple produced between the

steel and the plated deposit, the nature of the bath and other conditions used during production of the deposit.

Additional corrosion protection is obtained when a thin layer of copper or zinc is electrodeposited from a solution with additives^{8,9}; coating thickness has also been shown to be important. The results from the present investigation agree with these observations; increased corrosion protection has been afforded by the thicker coating, in the case of the sulphamate-based materials.

Previous work has also shown that copper deposits from nitrilotriacetate solutions⁷ (an alkaline non-cyanide bath) give marginally better corrosion resistance compared to cyanide baths, which show moderate protection. The present work confirms that the corrosion resistance of deposits from a sulphamate bath is better than obtained from cyanide solutions.

CONCLUSIONS

Polarisation, A.C. Impedance and weight-loss measurements lead to the same conclusions regarding the corrosion resistance of copper deposits obtained from different baths under optimised composition and plating conditions. The corrosion resistant nature of the deposits follow the order,

sulphamate>cyanide>EDTA.

The copper deposited on brass obtained from acids-sulphate also shows high corrosion

resistance. The corrosion resistance offered by the samples deposited from the sulphamate bath may be due to their uniform and fine-grained structure. Since its corrosion resistance is superior to the deposit produced from cyanide baths, the use of sulphamate baths are more advantageous on toxicity grounds.

ACKNOWLEDGMENTS

The authors would like to thank the Director, CECRI, Karaikudi, for permission to carry out this work and for his encouragement. One of the authors, P.Kokila, thanks the managing committee, Vivekananda College, Agasteeswaram for encouragement.

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