Bulletin of Electrochemistry 14 (10) October 1998, pp 320-325

0256-1654/98/$ 3-50

COPPER DEPOSITION FROM PERCHLORATE-BASED ELECTROLYTES

S SRIVEERARAGHAVAN, P SILVESTER, RM KRISHNAN, SOBHA JAYAKRISHNAN
S R NATARAJAN AND K BALAKRISHNAN

Central Electrochemical Research Institute, Karaikudi - 630 006, INDIA

[Received: 13 August 1998 Accepted: 4 September 1998]

Copper is electroplated for a wide variety of applications with the electroplating being carried out normally from cyanide or acid sulphate solutions. Experimental observations during the development of a perchlorate-based copper plating solution suggest that this electrolyte might be useful in industrial electroplating.

Keywords: Copper electrodeposition, optimum compositioin, perchlorate electrolyte.

INTRODUCTION

Electrodeposited copper generally serves as a preplate for the subsequent deposition of the desired metal on steel surfaces. It is also used to prevent case hardening on selected areas of ferrous metal surfaces. High speed cyanide copper is employed to produce heavy coatings of copper on steel wires for electrical applications. A copper coating is sometimes oxidised to produce an antique type finish. Other applications include electroforming, electrorefining and the manufacture of copper powder. Copper is normally deposited from cyanide and acid electrolytes. Among the acid-type electrolytes, the sulphate baths are preferred. The grain structure of copper deposits from a plain acid sulphate electrolyte is not very fine when compared with the structure from cyanide electrolytes. Electrodeposition of copper from perchlorate-based electrolytes does not find adequate description in published literature [1,2,3]. In this article an attempt is made to give a detailed description of copper deposition from perchlorate solutions.

EXPERIMENTAL

Hull cell studies were carried out on polished copper cathodes of 100 x 75 x 0.25 mm size with a cell current of 1 A and 2 litre solutions of varying compositions and operating parameters as indicated below.

Copper as perchlorate: 15.9 - 31.8 g/l, Perchloric acid: 50.2 - 100.5 g/l, Temperature: 303-323 ± 1 K.

The temperature was maintained by using a water bath. A regulated power supply served as the current source.

The electrolyte was prepared by dissolving the required amount of cupric oxide in perchloric acid and making up the solution to the required volume. Electrolytic copper was used as the anode.

The cathode efficiency studies were carried out on 50 x 40 x 1 mm copper cathodes mounted on jigs with anodes on either side of the cathode. The current efficiency was calculated from the mass gain of each specimen. From the values of the cathode efficiency the average rate of build-up and thickness were calculated.

The Vicker's microhardness of the copper deposits obtained under different conditions were determined by using a PMT-3 Russian made microscope hardness meter and a load of 25 g. Microhardness values (H_v) were calculated using the equation

$$H_v = 1854 \times L/d^2$$

L being the load in gm and d the diagonal in μm.

The structures of deposits were examined through a Scanning Electron Microscope of JEOL-JSM-35LF model, with a voltage range of 25 KV and for magnifications of 1000. The results obtained were compared with those of conventional acid and cyanide electrolytes.

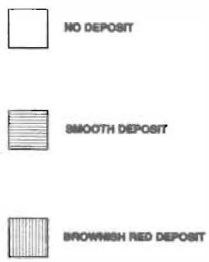

Fig. 1: Legend for Hull cell patterns

RESULTS AND DISCUSSION

Results of Hull cell studies

Effect of concentration of copper

Fig. 1 shows the codes used for recording the Hull cell patterns. Fig. 2 and Table I show the various Hull cell patterns obtained on a copper substrate at different temperatures for a cell current of 1 A and a duration of five minutes. In this series of experiments, a concentration of 100.5 g/l of perchloric acid was maintained. The patterns show mainly deposits with two characteristics, namely, (i) smooth red layer and (ii) dark reddish brown deposits. From Fig. 2, it is clear that the current density for the desired smooth red deposit ranges from 0.2 to 6.1 A/dm^2. The current density range for such deposits is maximum at higher temperatures, namely, 313 K and 323 K (0.1-6.1 A/dm^2) when compared to 303 K. However, this effect of temperature is not realised for the higher concentration of copper i.e. at 31.8 g/l, for which the range only decreases at 313 K. Generally, the desired current density range is not much altered by increasing the concentration of copper at any temperature, except at higher concentrations of copper and at 313 K.

TABLE I: Effect of variation of copper concentration in Hull cell tests

Bath Cu g/l	Composition $HClO_4$ g/l	Temp K	Cell current A	Range of current density for red layer A/dm^2
15.9	100.5	303	1	6.1 - 0.2
15.9	100.5	313	1	6.1 - 0.1
15.9	100.5	323	1	6.1 - 0.1
31.8	100.5	303	1	6.1 - 0.2
31.8	100.5	313	1	6.1 - 0.3
31.8	100.5	323	1	6.1 - 0.2

From the above series of experiments indicating a lack of any wide variation in the pattern of deposits with the increasing concentrations of copper, it was considered worthwhile to conduct further experiments, at a lower concentration of copper, viz., 15.9 g/l.

Effect of change of concentration of perchloric acid in solutions

Figs. 3 and 4 and Table II show the results obtained for different concentrations of perchloric acid at a copper concentration of 15.9 g/l and at different temperatures. From the figures it may be observed that the increase in concentration of perchloric acid up to 75.3 g/l reduces the range for smooth red layer to a minimum of 1 A/dm^2 at 303 K and later increases the range to the level as expected (6.1 to 0.1 A/dm^2, a wide coverage) for different temperatures till the concentration of perchloric acid is

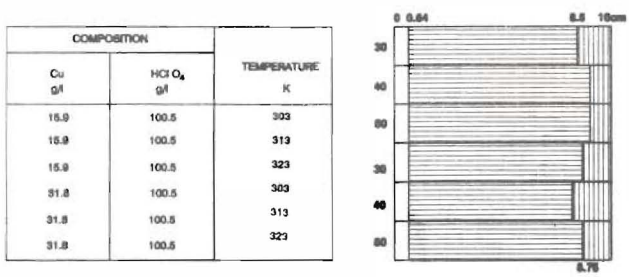

Fig. 2: Deposition pattern obtained from solutions composed of 15.9 g/l Cu and 100.5 g/l $HClO_4$

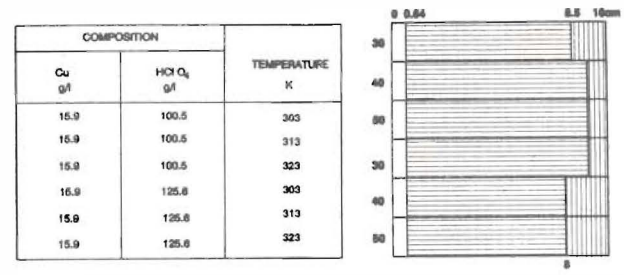

Fig. 3: Deposition patterns obtained from solutions composed of 15.9 g/l Cu and 50.2 - 75.3 g/l $HClO_4$

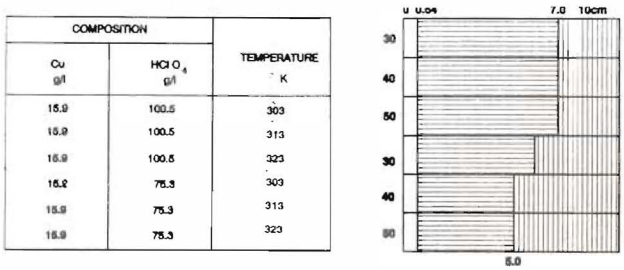

Fig. 4: Deposition patterns for solutions composed of 15.9 g/l Cu and 100.5 - 125.6 g/l $HClO_4$

reached to 100 g/l (Table II). This increase in perchloric acid concentration decreases the current density range for smooth red deposit to a minimum of 0.4 A/dm^2 with 125.6 g/l of perchloric acid and at 313 K and 323 K.

A full coverage of a smooth red deposit was indicated for concentrations of 15.9 g/l of copper and 100 g/l of perchloric acid, for temperatures up to 323 K and also for 15.9 g/l of copper and 125.6 g/l of perchloric acid for a temperature of 303 K. Hence, the optimum composition for a smooth red deposit was found to be one with 15.9 g/l of copper and perchloric acid, 100.5 g/l.

TABLE II: Effect of variation of perchloric acid concentration in electrolyte containing 15.9 g/l copper at 303 - 323 K

Bath Cu g/l	Composition $HClO_4$ g/l	Temp K	Cell current A	Range of current density for red layer A/dm^2
15.9	50.2	303	1	6.1 - 0.7
15.9	50.2	313	1	6.1 - 0.7
15.9	50.2	323	1	6.1 - 0.7
15.9	75.3	303	1	6.1 - 1.0
15.9	75.3	313	1	6.1 - 0.5
15.9	75.3	323	1	6.1 - 0.5
15.9	100.5	303	1	6.1 - 0.2
15.9	100.5	313	1	6.1 - 0.1
15.9	100.5	323	1	6.1 - 0.1
15.9	125.6	303	1	6.1 - 0.1
15.9	125.6	313	1	6.1 - 0.4
15.9	125.6	323	1	6.1 - 0.4

TABLE III: Results of current efficiency experiments with different bath compositions at 303 K

Bath composition g/l		Current density A/dm^2	Theoretical deposit mass for 100% CE g	Actual mass of deposit g	Current efficiency %
Cu	15.9	1.0	0.1482	0.1482	100
$HClO_4$	100.5	1.5	0.2223	0.2223	100
		2.0	0.2965	0.2965	100
X	200	1.0	0.1482	0.1441	97.2
Y	100	1.5	0.2223	0.2206	99.3
		2.0	0.2965	0.2948	99.4
CuCN	22.5	1.0	0.1482	0.1232	89.5
NaCN	34.0	1.5	0.2223	0.2219	99.8
Free cyanide	7.0	2.0	0.2965	0.2884	97.2

X = $CuSO_4 . 5H_2O$ and Y = H_2SO_4

Current efficiency studies

Table III gives the results obtained for different baths at 303 K. Table IV indicates the results for 313 K for perchlorate-based baths at different current densities.

Table V gives the results of current efficiency studies on perchlorate baths at 323 K for different current densities.

From Table III, it is evident that the current efficiency is always a maximum of 100% for current densities in the range 1.0 to 2.0 A/dm^2 at 303 K for perchloric acid-based baths. However, the cathode current efficiency is lower for a sulphuric acid-based bath, 97.2% at 1.0 A/dm^2, and the lowest, 89.5% for the same current density with a cyanide bath at the same temperature. The current efficiency is more or less the same for the acid sulphate bath operated at 1.5 or 2.0 A/dm^2 at 303 K. However, with the cyanide bath, the current efficiency increases up to 1.5 A/dm^2 (99.8% at 1.5 A/dm^2) and beyond that level decreases to 97.2% at 2.0 A/dm^2 at 303 K.

TABLE IV & V: Results of current efficiency experiments with perchlorate copper bath at 313 K and 323 K

Bath Cu g/l	Composition $HClO_4$ g/l	Current density A/dm^2	Theoretical deposit mass for 100% efficiency g	Actual mass of deposit g	Current efficiency %
15.9	100.5	1.0	0.1482	0.1482	100
15.9	100.5	1.5	0.2223	0.2223	100
15.9	100.5	2.0	0.2965	0.2965	100

TABLE VI: Comparison of deposits from various copper baths

Bath composition g/l		Current density A/dm^2	Temperature K	Nature of deposit
Cu	15.9			
$HClO_4$	100.5	1.0	303	Smooth, red
		1.5	303	"
		2.0	303	"
		1.0	313	"
		1.5	313	"
		2.0	313	"
		1.0	323	"
		1.5	323	"
		2.0	323	"
X	200			
Y	100	1.0	303	Rough, red
		1.5	303	"
		2.0	303	"
CuCN	22.5			
NaCN	34.0			
Free				
Cyanide	7.0	1.0	303	Dark brownish
		1.5	303	deposit
		2.0	303	"

X = $CuSO_4 . 5H_2O$ and Y = H_2SO_4

From Table IV, it may be noted that the current efficiency of perchloric acid-based electrolytes is not affected by any increase of temperature, showing the stability of bath performance.

Table V includes the results for current efficiency studies carried out at 323 K. These data prove the high stable current efficiency, reliability and reproducible behaviour of perchlorate-based electrolytes in comparison with all of the other electrolytes over the current densities studied.

Effect of current density on nature of deposit

Table VI gives an account of the various types of copper deposits obtained from different baths at different current densities and different temperatures. From Table VI, it is clear that a good, smooth deposit can be obtained at different temperatures (303 K, 313 K, 323 K) and at different current densities of 1.0-2.0 A/dm^2 with the perchlorate-based electrolytes, whereas the appearance changes to rough red for the same current density range at 303 K with the acid bath. In marked contrast to these results, the nature of the deposit becomes much worse for the current density range of 1.0- 2.0 A/dm^2 at 303 K with the conventional cyanide bath.

TABLE VII: Rates of build-up of copper deposit in perchlorate, sulphate and cyanide baths at different current densities and temperatures

Bath composition g/l		Current density A/dm^2	Temperature K	Rate of build-up of deposit µm/h
Cu	15.9			
$HClO_4$	100.5	1.0	303	13.3
		1.5	303	19.9
		2.0	303	26.6
		1.0	313	13.3
		1.5	313	19.9
		2.0	313	26.6
		1.0	323	13.3
		1.5	323	19.9
		2.0	323	26.6
X	200			
Y	100	1.0	303	12.9
		1.5	303	19.8
		2.0	303	26.4
CuCN	22.5			
NaCN	34.0			
Free				
Cyanide	7.0	1.0	303	11.0
		1.5	303	19.9
		2.0	303	25.9

X = $CuSO_4 . 5H_2O$ and Y = H_2SO_4

Thus from the viewpoint of current efficiency, minimum possible copper concentration and performance, the perchlorate baths might well be useful in industrial practice.

Rate of build up of copper deposit during plating

Table VII lists the data on the rates of build-up for different baths at different current densities. It can be inferred that the build-up rate is in the order: perchlorate > sulphate > cyanide for the current densities studied, e.g., 13.29 µm/h from perchlorate, 12.92 µm/h from sulphate bath and 11.04 µm/h from cyanide bath respectively at 1.0 A/dm^2 and at 303 K. The rate of build up for the perchlorate based solution at higher temperatures for the small range of current densities (1.0 - 2.0 A/dm^2) was found to be unaffected. The above results confirm that the perchlorate- based solutions performed better than the conventional cyanide and sulphate baths.

Results of microhardness measurements

Table VIII gives microhardness values for electrodeposits from different baths. It can be noted that the Vickers microhardness values for deposits from perchlorate-based solutions range from 71 to 100 kg/mm^2 under different

TABLE VIII: Vickers microhardness values for deposits from perchlorate, sulphate and cyanide copper baths at different temperatures

Bath composition g/l		Current density A/dm^2	Temperature K	Deposit microhardness HV_{25}
Cu	15.9			
$HClO_4$	100.0	1.0	303	71
		1.5	303	83
		2.0	303	71
		1.0	313	85
		1.5	313	71
		2.0	313	83
		1.0	323	100
		1.5	323	80
		2.0	323	82
X	200			
Y	100	1.0	303	94
		1.5	303	100
		2.0	303	80
CuCN	22.5			
NaCN	34.0			
Free				
Cyanide	7.0	1.0	303	97
		1.5	303	94
		2.0	303	89

X = $CuSO_4 . 5H_2O$ and Y = H_2SO_4

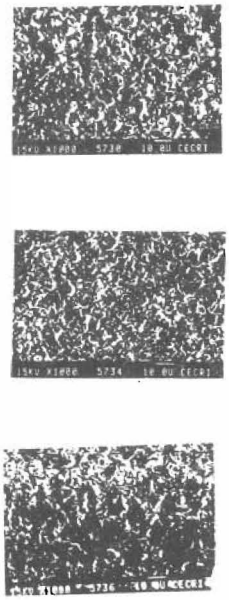

Fig. 5: SEM photomicrographs of copper electrodeposits prepared from perchlorate solution containing copper 15.9 g/l. perchloric acid 100.5 g/l at 1.5 A/dm^2 and (1) 303 K (2) 313 K (3) 323 K

Fig. 6: SEM photomicrographs of copper electrodeposits prepared from perchlorate solution containing copper 15.9 g/l. perchloric acid 100.5 g/l at 2 A/dm^2 and (1) 303 K (2) 313 K (3) 323 K

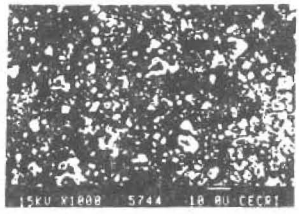

Fig. 7: SEM phoromicrograph of pure copper metal

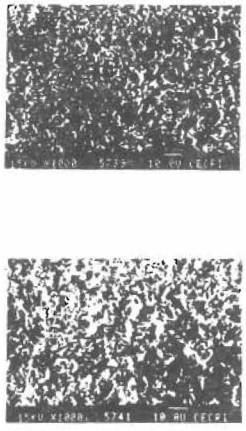

Fig. 8: SEM photomicrographs of copper electrodeposits from acid sulphate solution containing copper sulphate 200 g/l sulphuric acid 100 g/l at 303 K and (1) 1.5 A/dm^2 (2) 2.0 A/dm^2

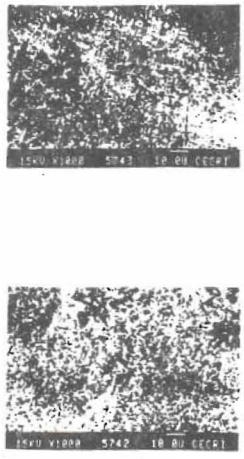

Fig. 9: SEM photomicrographs of copper electrodeposits from cyanide solution containing cuprous cyanide 22.5 g/l, sodium cyanide 34.0 g/l; free cyanide 7.0 g/l at 303 K and at 1.5 & 2.5 A/dm^2

conditions. The values are higher at higher temperatures (323 K) for different current densities besides being inconsistent at lower temperatures.

The microhardness values for perchlorate-and sulphate-based deposits do not follow any particular pattern and no general inference can be drawn.

In contrast, the microhardness values for deposits from the cyanide bath decrease with increasing current density.

Structure of deposits

Figs. 5-9 show the SEM photomicrographs of copper deposits produced from perchlorate, sulphate and cyanide solutions in comparison with pure copper metal. It is seen that copper electrodeposits with a uniform crystal pattern are obtained when the electroplating is carried out under varying current density and temperatures from perchlorate solution (Fig. 5).

CONCLUSION

From the studies carried out with different electrolytes, it is concluded that copper electrodeposits of acceptable quality can be obtained from perchloric acid-based electrolyte of the following composition

Copper: 15.9 g/l, perchloric acid: 100.5 g/l, current density: 1.0 - 2.0 A/dm^2, temperature: 303-323 K.

REFERENCES

1. F A Lowenheim (Ed), *Modern Electroplating,* 3rd Ed., John Wiley & Sons Inc., New York (1974)
2. E R Fahy and W V Sternberger, *Metal Progress,* 47,278 (1948); 48, 1311 (1945)
3. G C Tilburg, *Plating Surf Finish,* 71-6, 78 (1984)