Bulletin of Electrochemistry 17 (3) March 2001, pp 137-140 0256-1654/2001/$ 3-50

PERFORMANCE CHARACTERISTICS OF DIFFERENT FORMS OF ANODES IN COPPER ELECTROPLATING

S SRIVEERARAGHAVAN, RM KRISHNAN, SOBHA JAYAKRISHNAN
S R NATARAJAN, K MURUGADOSS AND C V RAMANAN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 03 May 2000 Accepted: 11 December 2000]

The performance of anode is of considerable importance in determining the success of an electroplating process. Usually anodes used for electroplating are of two types namely (i) soluble and (ii) insoluble. Mostly soluble anodes are used in almost all the plating electrolytes in view of maintaining the concentration of cations as required. However under certain critical conditions, it becomes a must to use insoluble anodes. Such characteristically significant anodes, behave differently in the baths when their position, size, shapes etc. are changed. This aspect is not elaborately investigated and reported in the literature. Investigations were carried out in the conventional cyanide and acid copper baths using soluble as well as insoluble anodes of different shapes and sizes and the results are reported in this paper.

Keywords: Copper electroplating, insoluble anodes

INTRODUCTION

Electroplating is employed in almost every branch of manufacturing industry for the application of metallic coatings onto articles made from metals in order that the surface may have properties which differ from those of the substrate and to non metallic products, most usually plastics, to provide metallic outer coverings [1]. Based upon the properties of metallic coatings, different metals are applied on different substrates like zinc or tin on steel for decorative look and corrosion protection chromium as thin layer for aesthetic appeal and as thick coatings for resistance to heat, wear and abrasion, silver/copper for high electrical conductivity, tin/lead for improved solderability etc.,

From the view of the versatile properties and uses [2] of copper like high electrical conductivity, as a masking agent during nitriding/carburising as a thermally conducting bottom coating for s.s. kitchen utensils, electroformed foils etc., it was considered to carry out the present investigations in copper baths.

Although electroplating is carried out successfully in the industry for various applications, it has been found that deposits obtained are of non uniform thickness distribution in most of the cases. To have a satisfactory performance for various functional applications like wear resistance, corrosion resistance, heat resistance etc., it is most essential that the deposits be of uniform thickness. Metal distribution depends on the shape and dimensions of the object and anode, the geometry of the plating cell arrangement, the conductivity of the bath, the shapes of the polarisation and current density curves, and the effect of agitation of bath [3]. Anode shape has a direct influence over its surface area and through this the uniformity of corrosion, the final scrap loss, the dispersal of gas from its surface and the tendency to polarise [4-5].

EXPERIMENTAL

The electrolytes used for the deposition of copper are the acid sulphate and the cyanide baths [6].

Preparation of electrolytes

For all the experiments, volume of the electrolyte prepared and used was 750 ml in a 1 litre corning glass beaker and the electrolyte prepared was as follows:

About 500 ml distilled water was taken in a one litre beaker and heated to lukewarm temperature. To this the required quantity of acid/cyanide salts added, for example in the case of cyanide baths, initially required quantity of sodium cyanide was added and later required quantity of copper cyanide was added and the solution was stirred continuously until all the salt dissolved; then the required quantity of sodium carbonate was added and then made upto 750 ml with distilled water. Bath composition used are as follows:

Acid bath

Copper sulphate	200 g/l
Sulphuric acid	100 g/l

Cyanide bath

Copper cyanide	22.5 g/l
Sodium cyanide	41.5 g/l
Sodium carbonate	15 g/l

Fabrication of the anodes

The performance of the anodes were studied using two different materials, copper and graphite. The soluble copper anode was chosen as it is commercially used in electroplating of copper. The insoluble anode - graphite was chosen as it is used in certain cases where the chemical dissolution of the anode is to be minimised.

The anode designs were drawn on electrolytically pure copper sheets of thickness 0.5 mm and cut using a shear after leaving suitable allowance for cutting (Fig. 1).

One end of the available graphite rod was turned in a lathe. This end not only acted as a reference point but also as a surface at which the jaws of the lathe could hold the piece properly for further processing. Using a hacksaw the graphite rod was cut down to circular slabs of minimum thickness possible. The various anode designs were drawn on the slab and cut. The following anodes were fabricated and used.

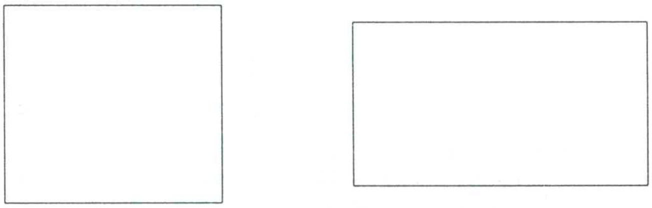
1. Equal area, square copper anodes
2. Equal area, circular copper anodes
3. Equal area, rectangular copper anodes
4. Equal area, triangular copper anodes
5. Equal area, square graphite anodes
6. Equal area, circular graphite anodes
7. Equal area, triangular graphite anodes
8. Lesser area, triangular copper anodes
9. Lesser area, triangular graphite anodes

Equal area means that the total effective area of the anode is equal to the cathode area and lesser area means total effective anode area is 50% of the cathode area.

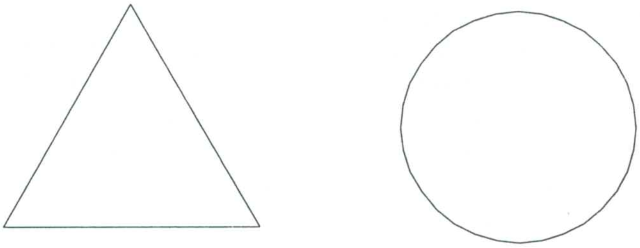
A cathode area of 5 x 5 cm^2 was chosen. With this given area the dimension of square, circular and equilateral triangular anodes were calculated. The side of square anode was 5 cm, the radius of circular anode 2.9 cm, the side of equilateral triangular anode 8 cm and the dimensions of rectangular anode 7.1 cm x 3.6 cm.

Sequence of plating

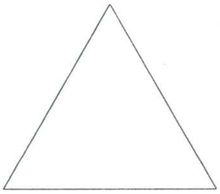
The cathodes used for the study were mechanically mirror polished, degreased with trichloroethylene, subjected to electrocleaning swilled with tap water, immersed in 5% (V/V) sulphuric acid for 15 seconds, again swilled and rinsed and then copper plated. Cyanide strike was done at 2 $A.dm^{-2}$ for 5 mts followed by plating from acid bath at 2 $A.dm^{-2}$ for 40 mts.



Square (Side 5 cm) Rectangular (3.6 x 71. cm)



Triangular (Side 8 cm) Circular (Radius 2.9 cm)



Triangular (Sides 5 x 5.6 x 5.6 cm)

Fig. 1: Anode designs used for experiments

Thickness of deposits from cyanide bath

In order to standardise the weight of deposit as well as the thickness obtained from cyanide bath, cathode specimens were copper plated for five minutes using each of the anodes separately at a current density of 2 A.dm^{-2}. Thickness of deposits were assessed from the weight gain using the equation,

$$\text{Thickness in microns } (\mu\text{ m}) = \frac{A}{B} \times 10^4 \qquad (1)$$

where A = Weight of deposit (gms) and B = Area of deposition x 8.92

Determination of current efficiency of acid copper plating bath

The pre-treated cathode specimen was first given copper strike in copper cyanide bath, swilled well with tap water, rinsed with distilled water and plated for 40 minutes from the acid copper bath, at 2 A.dm^{-2} and at room temperatures, using the different types of anodes. Then the current efficiency of the acid copper bath was calculated as follows:

$$\% \text{ Current Efficiency} = \frac{A}{B} \times 100 \qquad (2)$$

where A = Weight of deposit x 100 and B = Theoretical weight

Determination of thickness distribution

The thickness of deposit at various locations (9 positions) on both sides of the cathode (on two edges and middle portions of the cathode) was determined using a microtest thickness meter which is a magnetic gauge.

Determination of porosity

For determining the porosity of coatings of copper on mild steel substrates, the Ferroxyl test was used. The Ferroxyl solution used was one composed of Sodium chloride (NaCl) - 50 g/l and White gelatin - 50 g/l.

Filter paper strips of 10 mm x 10 mm area were impregnated with the above solution and placed at different locations on the plated surface. After 15 minutes, solution of 10 g/l potassium ferricyanide was spread on the filter papers. The porosity of each deposit was evaluated on the basis of the number of blue spots formed.

RESULTS AND DISCUSSION

Thickness of deposits from cyanide copper bath

From Table I, it can be observed that the thickness of the deposits from cyanide bath varies from 0.92 to 1.23 micron only when different anodes were used. This is only a thin layer of about 1 μ m given as an undercoat to avoid

TABLE I: Results of experiments carried out with different sized/shaped anodes in acid copper sulphate bath (Nature of deposit is Good, smooth and adherent)

Anode material	Anode design	Bath nature	Thickness (μ m)	C.E. (%)
Copper (sol)	square (equal area) (50 cm^2)	cyanide	0.94	X
"	"	acid	17.40	97.6
"	circular (equal area)	cyanide	0.92	X
"	"	acid	17.29	97.1
"	rectangular (equal area)	cyanide	0.98	X
"	"	acid	17.45	98.0
"	triangular (equal area)	cyanide	1.23	X
"	"	acid	16.74	94.0
Graphite (insol)	square (equal area)	cyanide	1.19	X
"	"	acid	16.63	93.3
"	Circular (equal area)	cyanide	1.23	X
"	"	acid	16.80	94.3
"	triangular (equal area)	cyanide	0.92	X
"	"	acid	17.05	95.7
Copper (sol)	triangular (lesser area)	cyanmide	1.11	X
"	"	acid	16.2	92.74
Graphite (insol)	"	cyanide	0.99	X
"	"	acid	17.40	97.67

immersion plating during plating from acid copper bath on mild steel base.

Current efficiency for deposition from acid bath

From Table I, it can be observed that current efficiency values at 2 $A.dm^{-2}$ for 40 minutes remain around 93-98% in the case of anodes of equal area irrespective of the nature and shape of the anode.

Distribution of thickness of deposits

From the values of thickness obtained on the cathodes using different size, shape and nature of the anodes, the actual distribution of the metal deposit on different positions on the cathodes were assessed. Typical results for two different anodes are shown in Tables II and III. From these and similar results obtained using other type of anodes it could be concluded that soluble anodes-square, rectangular and circular of equal area as that of the cathode, anodes with lesser area (both soluble and insoluble) and insoluble square anodes (equal area) fair better in producing more or less an uniform metallic coating on the cathode.

Porosity of deposits

From the ferroxyl test results it could be observed that all the deposits of thickness around 20 μm obtained independent of the type of anode used for plating are pore free.

TABLE II: Thickness distribution of copper deposits using lesser area triangular copper anodes

Position number	Plate 1 Side A	Plate 1 Side B	Plate 2 Side A	Plate 2 Side B	Plate 3 Side A	Plate 3 Side B
	Microns					
1	16	17	20	19	17	18
2	17	18	19	20	18	19
3	22	23	24	24	19	20
4	16	16	19	18	16	18
5	17	17	18	19	17	17
6	21	22	20	24	19	19
7	17	18	20	20	17	17
8	18	19	22	22	17	20
9	24	25	26	22	20	22

TABLE III: Thickness distribution of copper deposits using lesser area triangular graphite anodes

Position number	Plate 1 Side A	Plate 1 Side B	Plate 2 Side A	Plate 2 Side B	Plate 3 Side A	Plate 3 Side B
	Microns					
1	16	16	15	20	22	18
2	19	16	16	24	24	19
3	18	18	19	28	28	20
4	16	15	14	20	18	16
5	16	14	15	25	22	17
6	18	16	18	28	26	20
7	16	17	15	21	22	18
8	17	19	16	25	24	20
9	19	18	19	30	24	23

CONCLUSIONS

From the investigation carried out with different type of anodes, it is concluded that to obtain a more or less uniform deposit thickness distribution along with high current efficiency of deposition and adherent, smooth, and pore free deposit, the following 6 types of anodes can be used

- Soluble or insoluble square type of anodes with equal area as that of the cathode
- Soluble circular anodes of equal area as that of the cathode
- Soluble rectangular anodes of equal area as that of the cathode.
- Soluble and insoluble triangular anodes with 50% lesser area as that of the cathode

It is to add here that the use of triangular anodes with lesser area (50% lesser than the cathode) may lead to a remarkable effect in reducing the cost of the anodes and minimising the impurities build up, but with maintenance of required properties like uniform metal distribution and current efficiency.

REFERENCES

1. S Sriveeraraghavan, *Ph D Thesis submitted to Punjab University,* Chandigarh (1991)
2. Kobert Allen, *Finishing Handbook and Directory,* Sawell Publications, London, pp 122-133 (1994)
3. L J Dumey (Ed), *Electroplating Engineering Handbook,* Fourth Edition, Van Nostrand Reinhold Publishing Company, Princeton, New Jersey (1984)
4. W Canning, *Handlook of Electroplating,* E & F N, Spot Ltd, Birmingham, Twentithird Edition (1982)
5. D J Fishlock, *Plating Anodes, Electroplating (India) 2,* (3) p 7-15 (1966)
6. F A Lowenheim, *Modern Electroplating, Third Edition,* John Wiley and Sons Inc, New York (1974)