Throwing Power of Copper Sulfate Plating Baths

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Throwing power is an important characteristic in through-hole plating and other processes. Its evaluation by measuring cathodic metal distribution in special cells (Hull, Mohler, Hering-Blum, etc.) gives numerical values which strongly depend on the design and absolute dimensions of particular cell. Experiments with 9 different plating baths at 5 current densities gave numerical values of throwing power which varied over quite narrow range: from 20 to 70 %. Therefore variations in actual copper plate thickness over the surface of real plated parts are much better represented by the product of solution conductivity and the slope of the polarization curve which changed from 0.1 to 10 cm, i.e. over two orders of magnitude.

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Introduction

Electrodeposition of copper from acid sulfate solutions is characterized by high current efficiency – practically equal to 100 per cent. Therefore the distribution of current and metal over the cathode surface always coincides and the measurements of local deposit thickness provide complete information on actual current distribution.

The results of quantitative evaluation of throwing power by means of various cells (Hull cell, Mohler cell, etc.) depend much more on geometric parameters (size and shape of the cell) rather than on the properties of a particular plating solution.

The contributions of electrochemical and geometric factors to current distribution are expressed by Wagner's number, W:

$$W = æ\left|\frac{dE}{di}\right| \Big/ L = k/L \tag{1}$$

Here $k = æ\left|\frac{dE}{di}\right|$,

æ is specific conductivity,

E is cathode potential,

i is cathode current density,

and L is geometric parameter (so called "characteristic length").

There are three following typical cases:

(1) $W >> 1$

(2) $W << 1$

(3) $0.1 < W < 10$

In the first case current (and metal) distribution is uniform even for plating solutions with very low throwing power (expressed in per cent). Similarly, in the second case actual current distribution coincides with primary distribution, i.e. there is no "throw", while the particular solution may even have very high throwing power. Only in the third case the positive effect of throwing power can be seen.

Thus, for the evaluation of expected uniformity of coating thickness over the surface of a particular plated object (i.e. for L = const) throwing power in per cent seems to be less valuable than numerical values of electrochemical parameter. A comparison of throwing power (expressed in per cent), and k values for a number of copper sulfate baths has been made in the present paper.

Experimental

Throwing power was measured in a Mohler slot cell using 5-sections cathode (Fig.1).

Throwing power (TP) was calculated in the following way:

$$TP = \frac{\sum_{n=1}^{5} |a_n - b_n|}{\sum_{n=1}^{5} |a_n - 1|} \cdot 100 \qquad (2)$$

where a_n is primary current density on a given section $i_{n,pr}$, divided by its average value: $a_n=i_{n,pr}/i_{av}$, and b_n is secondary (actual) current density, $i_{n,sec}$ divided by its average value: $b_n=i_{n,sec}/i_{av}$.

Obviously, i_{av} is same in both primary and secondary current distribution.

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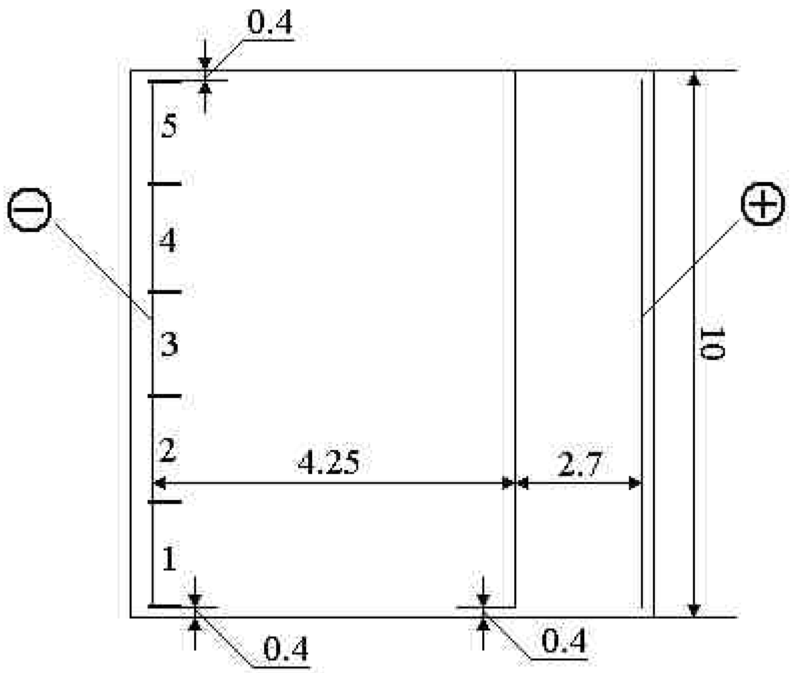

Fig. 1. Mohler cell for throwing power measurements. All dimensions expressed in centimeters.

Conductivity was measured using standard conductance cell and a.c. bridge. Values of dE/di were determined from polarization curves.

All experiments were made at 18-25 °C. Compositions of solutions tested are given in Table 1.

Table 1. Composition of copper plating solutions.

Component	Concentration of component								
	Solutions for plating parts					Solutions for plating PCBs			
	№1	№2	№3	№4	№5	№6	№7	№8	№9
$CuSO_4 \cdot 5H_2O$, g/L	200	2000	2000	2000	2000	80	80	80	80
H_2SO_4, g/L	50	50	50	50	50	200	200	200	200
NaCl, mg/L		40	40				40	40	40
HCl, mg/L				30	30				
Additives, ml/L: A		4	4						
B				3	3				
C							1	1	
D							8	8	
E									5
F									0.1

Results and Discussions

Data on cathode polarization, solutions conductivity, as well as calculated values of throwing power and k are given in Table 2.

All baths with high concentration of cupric ions and moderate concentration of sulfuric acid have throwing power within the range of 18 to 38 %. However k varies over much wider range – from 0.1 to 0.8 cm, i.e. by 8 times. This means that in geometrically similar systems (1) and (2) with L_1/L_2=8 same current and metal distribution will be observed.

It follows also from these data that uniform current and metal distribution should be observed on shaped parts of relatively small size: 0.01 to 0,1 cm respectively. It should be noticed that none of these conclusions could be made on the basis of numerical values of TP (18 or 38 per cent). Appreciable increase in k at lower current density ($\leq$0.005 A/cm^2) suggests somewhat better metal distribution in small recesses (of mm scale) in comparison with that expected from average k values.

Copper plating baths used in the manufacture of PCBs are characterized by 1.5 to 2 times higher throwing power. However the difference between k for the two groups of baths is much more pronounced - up to two orders of magnitude. This explains, why these baths are successfully used in through-

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hole plating and in other processes where uniform metal distribution is essential.

Table 2.

Bath №	i,A/cm^2 · 10^2	dE/di, V · cm^2/A	æ, Ohm^{-1} · cm^{-1}	k, cm	TP, %
1	0.5	2.4	0.161	0.386	21
	1	1.4	0.161	0.225	20
	1.5	1.0	0.161	0.161	19
	2	0.8	0.161	0.129	19
	3	0.6	0.161	0.097	19
2	0.5	3.0	0.161	0.483	25
	1	1.6	0.161	0.255	20.5
	1.5	1.0	0.161	0.161	20.5
	2	0.8	0.161	0.129	18.5
	3	0.8	0.161	0.129	18.4
3	0.5	4.6	0.161	0.741	31.5
	1	2.0	0.161	0.322	28
	1.5	1.0	0.161	0.161	25
	2	0.8	0.161	0.129	22.5
	3	0.8	0.161	0.129	21.5
4	0.5	2.6	0.161	0.419	30.5
	1	2.4	0.161	0.386	28.5
	1.5	0.6	0.161	0.103	18.8
	2	0.6	0.161	0.097	18.2
	3	0.4	0.161	0.129	-
5	0.5	4.8	0.161	0.773	36.7
	1	2.0	0.161	0.322	28.5
	1.5	1.6	0.161	0.258	28
	2	1.2	0.161	0.193	27.1
	3	0.8	0.161	0.129	-
6	0.5	2.6	1.121	2.915	31.9
	1	1.0	1.121	1.121	28.3
	1.5	1.0	1.121	1.121	28.5
	2	1.0	1.121	1.121	29
	3	2.4	1.121	2.690	-
7	0.5	6.6	1.121	7.399	66
	1	4.6	1.121	5.157	60.2
	1.5	4.8	1.121	5.380	60.5
	2	4.4	1.121	4.932	59.9
	3	9.6	1.121	10.760	-
8	0.5	9.2	1.121	10.310	68.5
	1	5.2	1.121	5.829	66
	1.5	4.8	1.121	5.380	63.5
	2	5.4	1.121	6.053	64.7
	3	10.2	1.121	11.434	-
9	0.5	10.6	1.121	11.800	68
	1	5.2	1.121	5.829	57
	1.5	5.2	1.121	5.829	55
	2	5.0	1.121	5.605	55
	3	7.6	1.121	8.519	-

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Summary

Throwing power as a characteristic of plating solutions and operating conditions (temperature, current density) measured by means of specially designed cells (Hull, etc.) is strongly effected by geometric parameters of these cells. Much better evaluation of throwing properties gives the electrochemical parameter k in the expression for Wagner's number.

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