Microstructure & Other Properties of Pulse-Plated Copper for Electroforming Applications

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Microstructure, hardness, material distribution and current efficiency were studied for various pulse patterns (both direct current, on/off and pulse reverse plating) and different bath compositions of copper sulfate and sulfuric acid, with additions of chloride. The objective was to develop a reliable copper electroforming process to provide a fine-grained and hard (above HV 125) deposit with good micro- and macrothrowing power. Potential applications include solar cell panels, tools for micro injection molding and various microelectromechanical systems (MEMS).

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Introduction

Electrodeposition of copper is one of the most frequently used processes within the field of surface finishing - both in terms of applications and amount deposited. Electroforming in copper, is only a region in the copper electroplating area, and includes all applications in which the deposited layer becomes the finished product itself. Examples of electroforming applications are; spark erosion tools, rocket engines [1] and printing equipment.

Recently, a line of new applications for copper electroforming has emerged in the area of micro-electromechanical systems (or MEMS). These include; plating of solar cell panels [2], support structures in tool inserts for micro-injection molding [3] as well as electromechanical structures in MEMS devices (such as sacrificial layers for fabrication of free-standing beams [4]).

Pulse Plating

All the different types of pulse plating used in this study can be expressed as variations of a general pulse waveform (Figure 1). To completely characterize the waveform, a number of parameter must by defined. In the general waveform two cathodic current densities, called i_{c1} and i_{c2}, are used. The relationship between the two current densities are expressed through a constant, y, as:

$$i_{c2} = y\, i_{c1} \tag{1}$$

If y is zero, current is switched on and off during the cathodic period of the waveform. If y is 1, there is only one level of cathodic current density (i.e. ordinary pulse reverse plating). And if y is between zero and 1 we have what is sometimes referred to as a pulsed pulse reverse [5] waveform (Figure 1).

In the cathodic period the current level i_{c1} is kept for T_{c1} milliseconds followed by i_{c2} for T_{c2} milliseconds and this is repeated x times.

The anodic period follows immediately after the cathodic period. The variable z is used to describe the level of the anodic current density:

$$i_a = z\, i_{c1} \tag{2}$$

One of the most important parameters in pulse reverse plating is the ratio between the anodic, Q_a, and cathodic, Q_c, charge:

$$\frac{Q_a}{Q_c} = \frac{i_a T_a}{(i_{c1} T_{c1} + i_{c2} T_{c2})\, x} \tag{3}$$

The average current density, i_{av}, is calculated as total charge, $Q=Q_c-Q_a$, divided by the total time, $T=T_c+T_a$, of a waveform:

$$i_{av} = \frac{(i_{c1} T_{c1} + i_{c2} T_{c2})\, x - i_a T_a}{(T_{c1} + T_{c2})\, x + T_a} \tag{4}$$

In the present study pulse waveforms with average current densities of either 2.00 or 4.00 A/dm^2 have been used, as well as DC experiments at the same current densities.

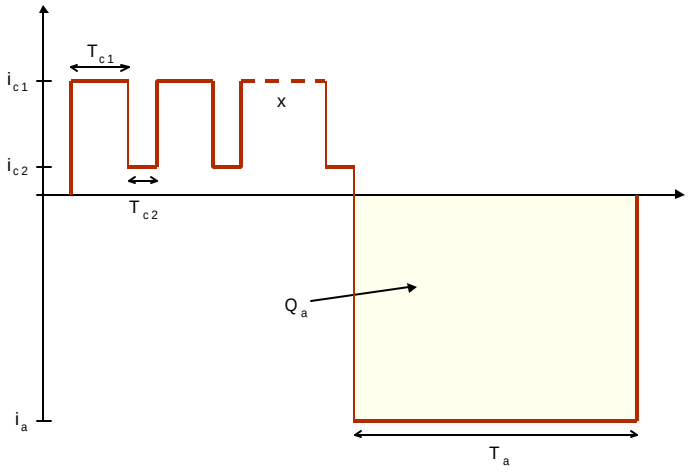

Figure 1: General pulse waveform with some of the parameters used to describe it.

Experimental

In current efficiency calculations, compensations for rectifier offset have been included. For any rectifier there is an offset value, typically a small percentage of the maximum output of the rectifier. The inaccuracy of the rectifier used in our experiments (a ±20 A computer controlled pulse reverse rectifier from TCD Teknologi ApS) can be expressed as:

$$I_{output} = 0.999 \cdot I_{input} - 0.0526$$

Taking this formula (derived from a series of current measurements at different levels) for the rectifier inaccuracy into account, the total charge delivered in i.e. exp. 4T5 is 9851 C. Since 4T5 lasted 7200 seconds with an average current of 1.4 A, the total charge for the experiment should be 10080 C.
The shape of pulses used has also been tested (using an oscilloscope), and was found to be very close to the expected square waves.

Pre-treatment and Electrolyte

Experiments were carried out on rolled polycrystalline copper substrates, cut into coupons measuring 50x50x5 mm. The pre-treatment procedure for the substrates is given in Table 1.

Table 1: Pre-treatment procedure

Polishing	320-500-1000-4000 grid wet SiC-paper was used for the metallographic preparation
Degreasing	Cathodic electrolytic rinse[1], 4 V, 2 min. at R.T.
Chemical polishing	MECUZID[2], 1 min. at R.T.
Degreasing	Cathodic electrolytic clean, 4 V, 2 min. at R.T.
Drying and weighing	
Back coverage	3M chemically resistant tape
Pickling	Ammoniumpersulfate[3], 2 min. at R.T.

The cell used for electrodeposition was built for this study, based on previous experience in MEMS and interconnect plating [2, 4]. Freshly filtered (1 µm mesh cartridge-filter) electrolyte was pumped continuously towards the cathode surface through a directed nozzle. All fixtures for the electrodes were machined out of pure copper to avoid any contamination of the electrolyte. A titanium basket mounted in a fine-woven polypropylene bag and filled with P-alloyed copper rounds, served as anode.

The electrolyte used was similar to that of Tajiri and Imamura [1], containing only $CuSO_4$, H_2SO_4 and Cl^- (Table 2).

Table 2: Electrolyte composition. To the amount of chloride found in the copper sulfate concentrate, sodium chloride was added to a total chloride concentration of 40 ppm.

Bath constituent	Amount
$CuSO_4 \cdot 5\ H_2O$	140 g/l
H_2SO_4	140 g/l
Cl^- (added as NaCl)	40 mg/l

The electrolyte was agitated using compressed air, and operated at room temperature. The total volume was 22 liters (5.8 gal).

[1] Cathodic rinse electrolyte: 15 g/l Na_2CO_3 , 15 g/l NaCN, 50 g/l NaOH
[2] 400 ml MECUZID SBM 200 from Chembo A/S (DK) + 400 ml H_2O + 20 ml H_2O_2 (always freshly mixed)
[3] 50 g/l $(NH_4)_2S_2O_8$

Initial Experiments

From the literature four different types of pulse plating were selected, along with a DC reference. In the initial experiments the average current density was 2.00 A/dm^2.

P1: For electroforming of copper a slow pulse reverse waveform, with T_c = 20 s and T_a = 4 s, was proposed by Tajiri & Imamura [1]. The cathodic and anodic current densities are identical (i.e. z equals 1.0).

P3: A much faster pulse reverse waveform, inspired by electroforming of nickel [4], was also selected. T_c = 60 ms, T_a = 20 ms, z = 1.5 and Q_a/Q_c = 0.5.

P4: High frequency on/off plating is known to enhance fine-grained growth. To investigate on/off plating a waveform with T_{c1} = 8 ms and T_{c2} = 2 ms (y = 0) was used [6].

P5: A pulsed pulse reverse waveform adapted from Leisner [5], consisted of two alternating cathodic levels repeated 500 times (i.e. x = 500) with $T_{c1} = T_{c2}$ = 20 ms (y = 0.4) and a strong anodic pulse with T_a = 500 ms and an anodic current density 5 times higher than i_{c1} (z = 5.0).

Taguchi Experimental Planning

In order to investigate the influence of each of the different parameters in the general pulse waveform, a systematic experimental plan was scheduled according to the Taguchi method [7].

Table 3: Taguchi experimental plan for the T-series of experiments. T_a is in milliseconds.

Exp.	Q_a/Q_c	T_a	y	z
4T1	0.1	100	0.0	1.0
4T2	0.1	500	0.4	1.5
4T3	0.1	4000	1.0	2.5
4T4	0.2	100	0.4	2.5
4T5	0.2	500	1.0	1.0
4T6	0.2	4000	0.0	1.5
4T7	0.3	100	1.0	1.5
4T8	0.3	500	0.0	2.5
4T9	0.3	4000	0.4	1.0

With the values for the investigated parameters listed in Table 3, it is possible to calculate i_{c1}, x, i_{c2} and i_a (by solving equations 1 through 4) when T_{c1}, T_{c2} and i_{av} are fixed.

For all the experiments in the Taguchi series an average current density, i_{av}, of 4.00 A/dm^2 was used, and based on the results from the initial experiments (next section) T_{c1} and T_{c2} was fixed to 20 and 10 ms respectively.

Hardness Measurements

Micro-hardness measurements were conducted using a Vickers diamond and a load of 25 g ($HV_{0.025}$). The indentations were made on the polished cross-sections[1] (later used for thickness measurements, Figure 2) perpendicular to the surface of the cross-section. The indentations were made in the region of the deposit

[1] The cross-sections are made from a 10x10 mm big piece of the sample cut in the middle of the 50x50 mm large speciment.

closest to the substrate (to avoid influence from the mounting resin). The uncertainty has been calculated to be ±7 for the initial experiments (see Table 4) and ±5 for the rest of the experiments (mainly because the initial experiments were only half as thick).
The deposited copper consists of a columnar layer growing perpendicular to the substrate surface. Each hardness value reported, is an average of 5 measurements.

Macro Throwing Power

Since the objective of this investigation is to develop a process for electroforming, focus has been on hardness, ease of use (low maintenance, no additives), process stability and macro - rather than micro - throwing power.
Given the total area of the copper substrates (0.35 dm^2 or 5.43 in^2), the average thickness is calculated based on the weight gain. The ratio between actual thickness in the middle of the test panel and this average thickness is used to compare the macro throwing from specimen to specimen.
The macro throwing power ratio is calculated as:

$$\text{Ratio} = \frac{x_{min} + \frac{x_{min} + x_{max}}{2}}{x_{av}} \quad (5)$$

In which x_{min} and x_{max} are the minimum and maximum thickness measured on the polished cross-sections (see Figure 5) and x_{av} is the average thickness calculated from the weight gain. If the throwing power is "perfect" the ratio will be 2. The geometry of the substrate, with massive build-up on corners and edges, will lead to much lower ratios.

Current Efficiency

The current efficiency (CE) was calculated for each experiment as the difference (in percent) between the applied corrected (see above) charge passed and the measured weight increase.

Surface Roughness

The surface roughness was calculated as the maximum thickness measured (in micrometers) divided by the minimum thickness.

Results & Discussion

Initial Experiments

In the initial experiments a clear picture is seen in the current efficiency results. For DC and the slow (P1) pulse reverse experiments, the current efficiency (referred to as CE) is 97%, the very fast pulse reverse experiments (P3) has a CE of almost 100% while the pulsed pulse reverse (P5) and on/off plated were lowest (94-96%).

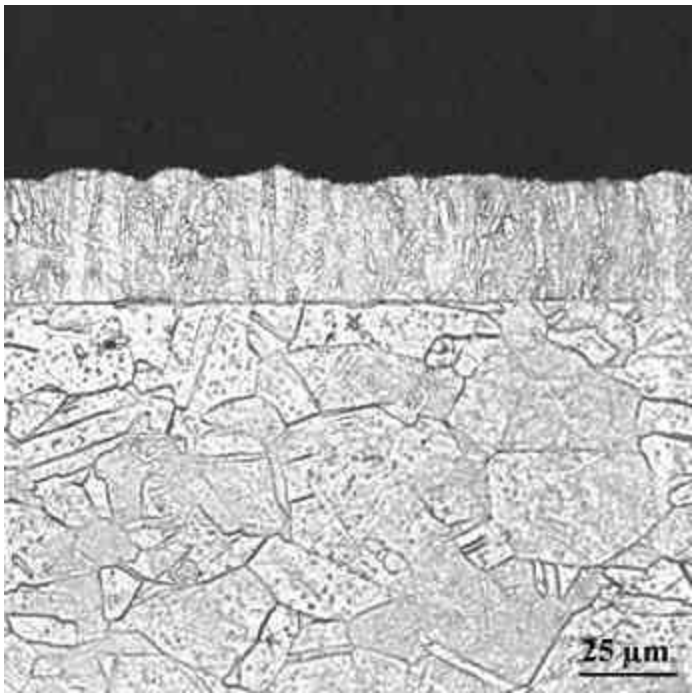

Figure 2: Polished cross-sections of direct current plated copper at 2.00 A/dm^2 (2DC). The line between the fine-grained deposit and the coarser substrate is obvious.

The hardest deposits were the pulse (and pulsed pulse) reverse plated specimens (around 125 HV), while both DC (90 HV) and on/off plating (HV 107) were softer. The fast pulse reverse waveform (called P3) gave an undesired rough or oxidized surface.

Table 4: Results from the initial experiments. The P3 pulse provided a good throwing power, but a rough deposit with large grains and hardness too low to measure.

		Deposit thickness		M.thrw.p.	
Exp.	CE	Minimum	Maximum	Ratio	Hardness
2DC	97.2	30.2	34.2	0.582	90
2P1	97.2	28.7	33.8	0.583	128
2P3	99.1	21.8	36.7	0.685	-
2P4	95.0	32.7	36.6	0.654	107
2P5	96.1	31.2	34.0	0.599	125
4P1	95.9	28.8	31.1	0.588	124
	%	µm	µm		HV

The ratio between calculated and measured (in the middle of the coupons) thickness, that is used to indicate the macro throwing power, did not change very much with the waveform used. Not surprisingly DC was lowest, while on/off plating (exp. 2P4) gave a significantly higher ratio than anticipated. Utilization of on/off plating at 100 Hz could be fast enough to anticipate some influence of the so-called capacity effect [8], which would explain this unexpected high ratio. Since pulse plating on an industrial scale (100 A or more) becomes very difficult at high frequencies, this issue has not been investigated further in this paper.

The conclusion, based on the initial experiments listed in Table 4, is that in order to obtain hard deposits pulse reverse plating such as P1 or P5 must be applied. Fast pulse reverse plating, as illustrated by P3, provides excellent current efficiency but poor appearance and coarse microstructure. On/off plating (P4) is not hard enough and furthermore exhibits the lowest current efficiency.
Consequently, the following experiments will be an optimization of the parameters that characterize pulsed pulse reverse plating. Based on P1 and P5, it was decided to optimize T_a, Q_a/Q_c, y and z - and to assign fixed values to T_{c1} (20 ms), T_{c2} (10 ms) and i_{av} (4.00 A/dm^2).

Taguchi Experiments

The results of a Taguchi experimental plan are usually presented as a curve for each of the investigated parameters showing the average result of the different levels. In this case, with four parameters on three levels, a point on a curve is calculated as the average of the three experiments carried out at that particular level. Studying the slope of the curves (Figure 3) gives an impression of the influence of a given parameter. A steep slope means that the parameter has a substantial influence on the result while a flat curve indicates no significant influence.

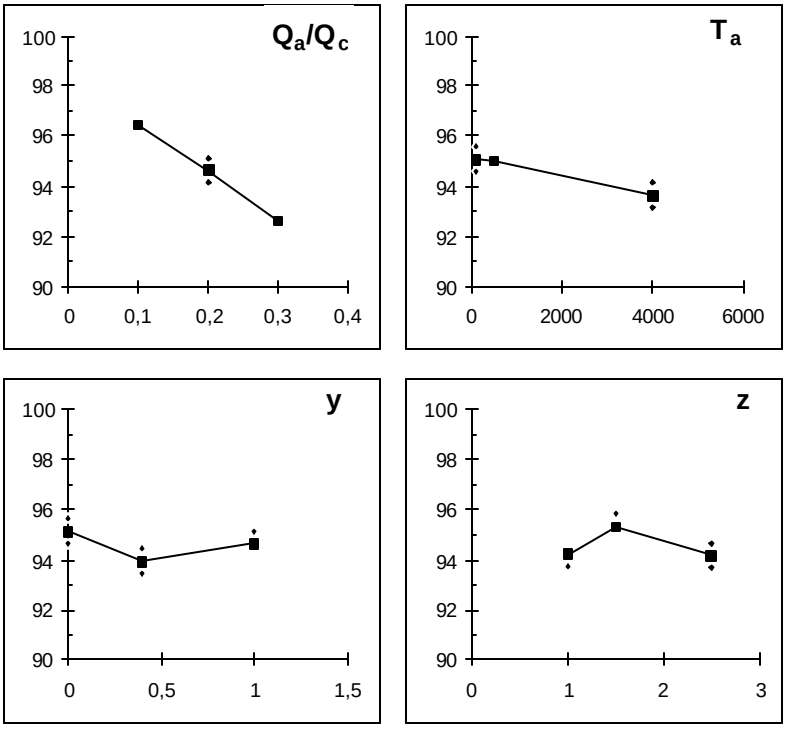

Figure 3: Current efficiency (CE) in percent as a result of the four parameters on three levels investigated in the Taguchi series (T1-T9).

In Figure 3 the ratio between anodic and cathodic charge, Q_a/Q_c, is the most important parameter influencing the current efficiency. Q_a/Q_c is responsible for 72% (not shown in the figure) of the variance, T_a is responsible for 12% while the influence of y and z are insignificant. The confidence level is ±0,5% (indicated as small dots above and below each point in Figure 3). The strong correlation between Q_a/Q_c and the current efficiency is somewhat surprising - and remains unexplained at present.

From the results of the hardness measurements for all the nine experiments in the Taguchi series, it is clear that the most important parameter is the anodic time, T_a, which is responsible for a little more than 50% of the variance. Also significant are y and z, while the influence of Q_a/Q_c on the hardness is insignificant (less than 5% of the variance). With a confidence level of 7 (Figure 4), it is not possible to quantify the influence of the ratio between anodic current density and cathodic current density, z. On the other hand, it seems as if y=0.4 (i.e. pulsed pulse reverse) is somewhat better than y=0 or y=1.

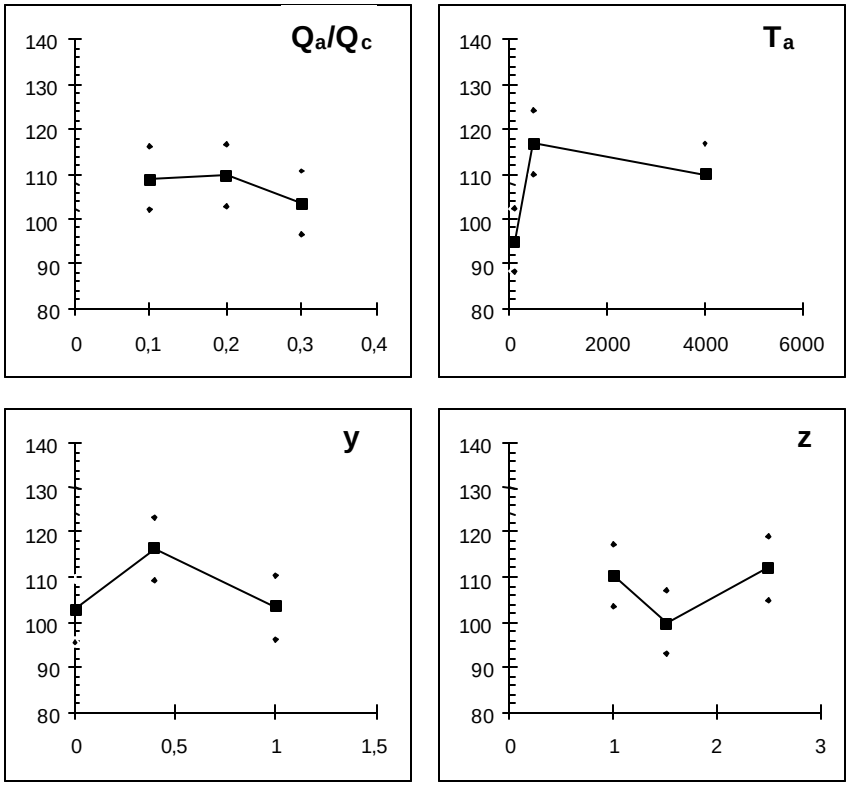

Figure 4: Hardness (micro Vickers, 25g) as a function of the three levels used for each of the four investigated parameters. The most significant parameter is clearly the anodic time, T_a.

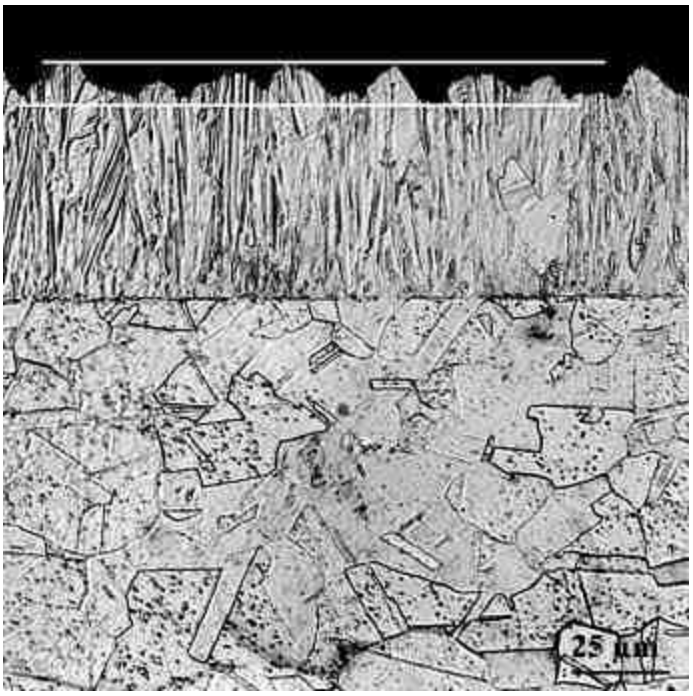

Figure 5: Polished cross-sections of 4T4. The maximum and minimum thickness, used to calculate the surface roughness and macro throwing power, are indicated by the horizontal lines.

The macro throwing power results of the Taguchi series (Table 5) does not lead to any obvious conclusions. All of the four parameters contribute to the variance, but the changes are small compared to the uncertainty of the measurements. There is no obvious connection between the Qa/Qc ratio and the throwing power, but is seems that switching between two cathodic current levels (y=0.4), yields a better throwing power than when y is zero or one. Two of the experiments with z=2.5 are relatively good (4T3 and 4T4) but the last z=2.5 experiment (4T8) is rather low as far as throwing power ratio is concerned, and this is enough to destroy the expected conclusion being that high z leads to improved macro throwing power.

Table 5: Results of the 9 experiments in the Taguchi series. The surface roughness is calculated by dividing the maximum with the minimum deposit thickness.

		Deposit thickness		M.thrw.p.	
Exp.	CE	Minimum	Maximum	Ratio	Hardness
4T1	95.1	47.6	62.9	0.566	95
4T2	97.2	56.2	61.7	0.586	120
4T3	95.2	54.3	57.4	0.566	112
4T4	94.1	49.1	62.1	0.570	111
4T5	94.8	46.8	54.7	0.515	118
4T6	95.0	51.3	54.5	0.543	100
4T7	93.9	50.5	62.0	0.576	80
4T8	93.2	49.5	52.7	0.537	113
4T9	90.7	52.3	55.8	0.574	118
	%	µm	µm		HV

The surface roughness expressed as the maximum thickness divided by the minimum thickness (Table 5) depends almost entirely on T_a (88% of the variance). In other words, of the 9 experiments 4T1, 4T4 and 4T7 are rough, while the rest of the deposits are relatively smooth. It seems that in the experiments with a T_a of 100 ms, large grains, rough deposits and low hardness values are obtained. The explanation to this observation, is probably that a certain amount of negative charge (or possible just a long off period) is needed to break the growth behaviour that leads to large grains (and the accompanying low hardness).

Final Experiments

A few experiments were performed to test the reproducibility, and trend indicated in the previous sections. Experiment 4T9 was repeated, this time having a hardness of 120 (compared to 118 in the first experiment, see Table 5). A direct current experiment at 4.00 A/dm^2, was harder (106 HV) than the one at 2.00 A/dm^2 (Table 4). This correlation between current density and hardness is known from the literature [1].

An additional experiment, similar to 4T2 but with y=0.6, showed a better throwing power ratio (0.597) compared to 4T2 but a lower hardness (112 HV).

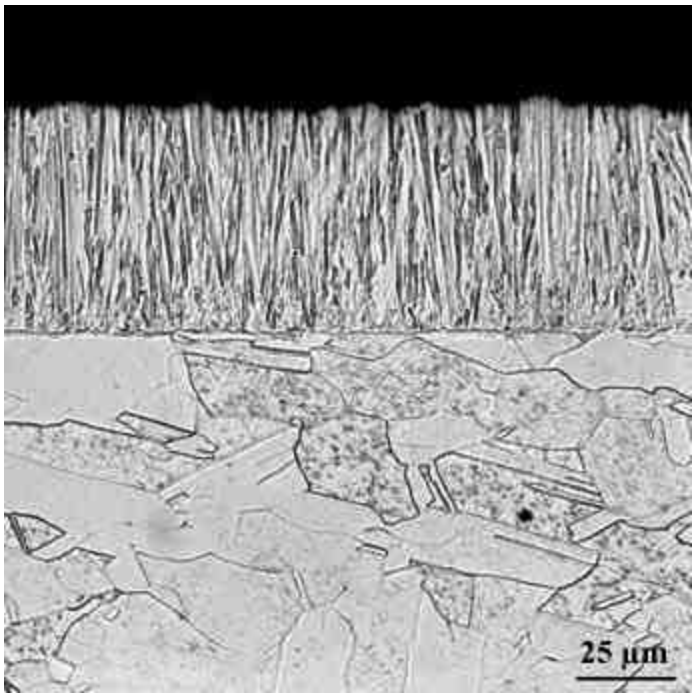

Figure 6: Pulse plated copper at an average current density of 4.00 A/dm^2 (4T2). The surface is semi-bright (silk-look) and the deposit has a columnar structure. The hardness is 120 $HV_{0.025}$.

Conclusion

It is possible, using pulse reverse plating, to deposit thick layers of copper, probably up to several millimeters, which is suitable for an electroforming process.
The deposits are relatively fine grained, with a columnar structure and hardness around 120 HV.
The process runs at room temperature in a very simple electrolyte without additives.
Hard and relatively smooth deposits can be obtained as long as the anodic period is 500 ms or longer. The current efficiency is from 97% (with a Q_a/Q_c of 10%) down to 91-94% for a Q_a/Q_c of 30%.
The macro throwing power is slightly improved by the pulse plating waveforms investigated, but some promising results using high frequency on/off plating need to be further investigated. In order to improve the throwing power significantly, as reported by Leisner [3], much higher Q_a/Q_c ratios must be applied, which will probably reduce the current efficiency.

Acknowledgement

The authors would like to thank the people at the department workshop, and especially laboratory technician Annemarie Ripa for preparation and documentation of the polished cross-sections.

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