Journal of Industrial Technology 5 (2), 1995, 51-60

EFFECT OF ADDITIVES ON THE ELECTROLYTIC DEPOSITION OF COPPER POWDER

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RINGKASAN: *Serbuk kuprum untuk kegunaan kajilogam serbuk, boleh dihasilkan melalui kaedah pemendakan elektrokimia. Tujuan penyelidikan ini adalah untuk mencari kesan ke atas kadar pemendakan serbuk, kecekapan proses dan arus dan struktur serbuk apabila bahan kimia tambahan dimasukkan ke dalam elektrolit asas. Kepingan kuprum dan plumbum tulen dijadikan anod dan katod masing-masing dan kepekatan elektrolit asas iaitu ion kuprum dan sulfat ditetapkan semasa ujikaji dijalankan. Bahan tambahan gliserin dan kuprik klorida didapati akan menambahkan kadar pembentukan serbuk kuprum dan kecekapan proses keseluruhannya. Struktur dendrit kelihatan di katod semasa ujikaji berjalan dan selepas dikisar didapati strukturnya berubah kepada flek dan nodul yang sesuai untuk kegunaan kajilogam serbuk. Analisis ke atas saiz serbuk dijalankan dan didapati taburannya adalah sama dengan taburan saiz serbuk yang diperolehi secara komersil di pasaran.*

ABSTRACT: Copper powder, for powder metallurgy applications, can be produced by electrochemical deposition method. This research work investigates the effect of powder deposition rate, current and process efficiency and powder structures through the addition of chemical additives into the mother liquor. High purity copper and lead were used as the process anode and cathode respectively while the concentration of copper ions and sulphate radicals were kept constant through out the experiment. The addition of glycerine and copper chloride as process additives were found to increase the deposition rate and the overall process efficiency. The generated copper particles were observed to have dendritic structure. Further processing produced flake and nodular particle morphology which were thought to be suitable for most powder metallurgy applications. Particle size analysis was done and an observation was made that the distribution lies within the commercially available sizes.

Keywords: Powder metallurgy, electrochemical deposition, current and process efficiency, chemical additives, dendritic, flake, nodular structures.

INTRODUCTION

Copper powder can be produced by various processes, categorically as the communication processes, chemical processes and the electrochemical processes (ASM handbook, 1984; EPMA, 1994). This paper discusses the electrodeposition of copper particles from acidified copper sulphate solution. It is known that this method produces high purity and dense particles and due to included hydrogen, it is brittle and can be readily sized by ball milling.

Commercially available copper powders produced by electrodeposition are classified into two types. Type 1 comprises of fine powders measuring -325 mesh having an apparent density of less than 1 gcm^{-3}. This type exhibited a fine branched crystal or dendritic in structure. Type 2 measures +325 mesh to -100 mesh powder having an apparent densities in the range of 2.5 to 2.7 gcm^{-3}. The latter are relatively more compact than the dendritic and is nodular in structure (Ralph, 1976).

In this experiment, a typical acidified copper sulphate solution was electrolysed with and without bath additives to observe the deposition efficiency, particle morphology and size distribution after milling. Peissker, (1991) suggested the following electrolytic composition:

Copper in copper sulphate	5 - 30 gl^{-1}
Sulphuric acid	150 - 25 gl^{-1}
Bath temperature	40 - 60°C
Applied voltage	1.0 - 2.0 Volts
Cathodic current density	600 - 4000 A m^{-2}
Anodic current density	300 - 600 A m^{-2}

The cathode material is either copper, aluminium or lead sheet while the anode material is pure copper.

Addition of bath additives greatly influences the particle shapes, sizes and process efficiency, while addition of chloride ions improves particle apparent density (Peissker, 1991). An improvement in the process efficiency, particle sizes and a variable of particles morphology were observed with an addition of increasing ratio of glycerine to cupric chloride solution.

MATERIALS AND METHODS

Mother Liquor Preparation

The original mother liquor was prepared as suggested by Peissker (1991), which has the following composition and operating conditions:

Copper in copper sulphate	26 gl^{-1}
Sulphuric acid	108 gl^{-1}
Anode and cathode current densities	1111 A m^{-2}
Bath temperature	50°C

Bath Additives

The following bath additives were prepared:

1. A five percent, volume by volume, glycerine solution was prepared by diluting analytical grade glycerine with deionised water.

2. A ten percent, weight by volume, of analytical grade cupric chloride was dissolved in deionised water.

Electrolytic Cell Set-up

Figure 1 shows the electrolytic cell set-up. Pure copper as an anode and pure lead as a cathode are connected to a direct current source as shown. The effective surface area of both electrodes at 36 x 10^{-4} m^2 were fully immersed in 800 cm^3 of the mother liquor. Agitation was done by magnetic stirrer and the temperature was kept constant at 50°C. Initially, electroposition was performed without additives and the subsequent electrodeposition was done with an increasing ratio of glycerine to cupric chloride. The electrodeposition was conducted for a suitable period of time to collect a quantity of copper particles.

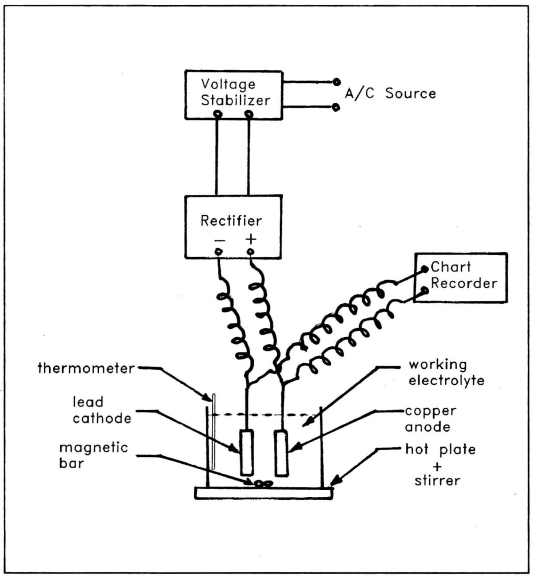

Figure 1. *The schematic diagram of the experimental set-up.*

The deposited particles on the lead cathode were brushed down to the bottom of the beaker hourly and was filtered and washed at the end of the electrodeposition period. They were then dried in a furnace, their weight was recorded and was further processed by ball grinding for particle size reduction. Sieving was done to obtain particle size distribution.

Powder purity analysis was done by using inductively coupled plasma (ICP) technique, while the particle morphology was analysed using scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The powder deposition rate

Figure 2 shows an individual effect of five and ten percent glycerine and cupric chloride solutions respectively. Both additives give an exponential rise in the deposition rate of copper powder. The overall process efficiency was observed to increase from 86 to 98 percent.

Figure 3 exhibits the combined effect of glycerine and cupric chloride on the copper powder deposition rate. It shows an increased amount of copper powder generated. An optimum ratio of glycerine to cupric chloride solution of about 10 was observed to give an optimum copper deposition rate of about 4.7 grams per hour. The corresponding overall process efficiency increased from 86 to about 99 percent.

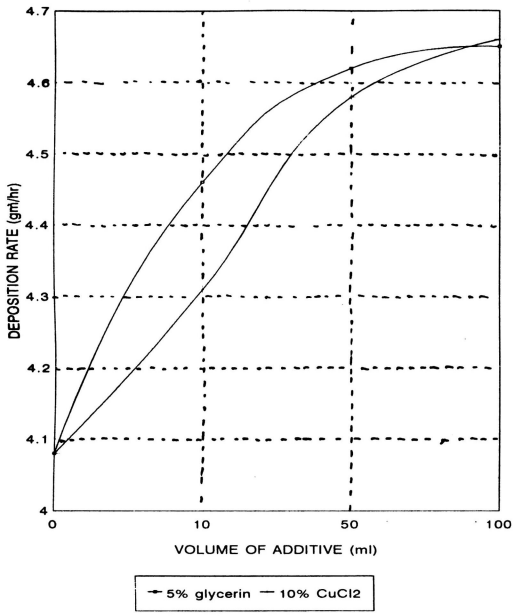

Figure 2. *Powder deposition rate versus volume of bath additives.*

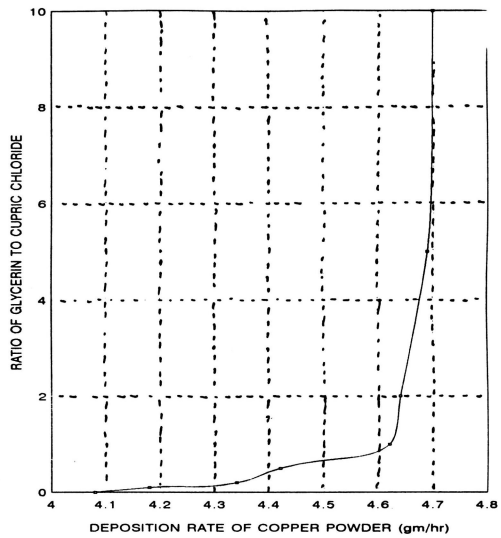

Figure 3. *Effect of additive ratios on powder deposition rate.*

Dendrites morphology and particle size distribution

Figures 4a through 4d show that the generated copper powder has a dendritic structure. Without additive, the generated copper powder developed into coarse and short sized dendrites. Through the addition of bath additives, elongated fine dendrites were obtained.

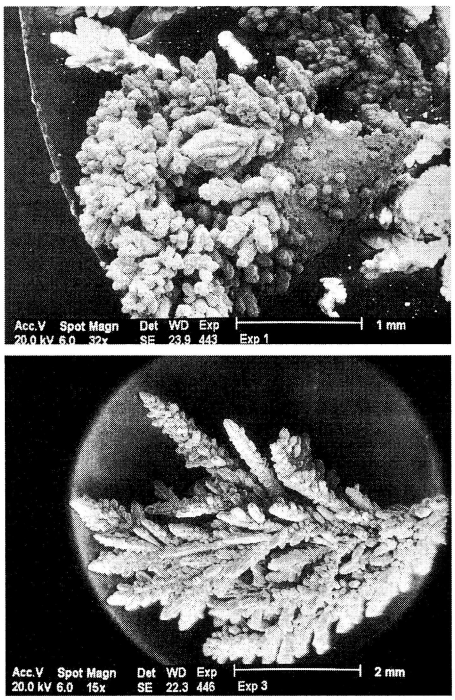

Figure 4a. *Scanning electron microscope (SEM) observations on dendrites formation.*
Above: without bath additives
Below: with 50 ml of glycerine

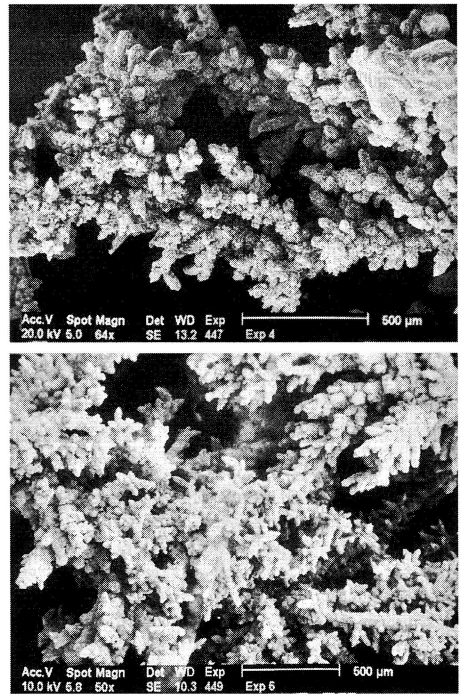

Figure 4b. *SEM observations on dendrites formation.*
Above: with 100 ml of glycerine
Below: with 50 ml of cupric chloride solution

Table 1 shows the particles size distribution in weight percentages after ball milling. It is observed that the distribution of coarse particles is higher than the fine particles. With the addition of glycerine and cupric chloride into the electrolyte, the ground particles distribution shows about 60 to 70 percent of weight percentages are greater or equal to 180 µm in size and about 30 to 40 percent of weight are particle size of less than 180 µm. The observed phenomenon is due to the increase in copper ductility and decrease of brittleness as the overall process efficiency escalated. Low hydrogen evolution which is responsible for embrittlement of copper deposits occurred with increased process efficiency.

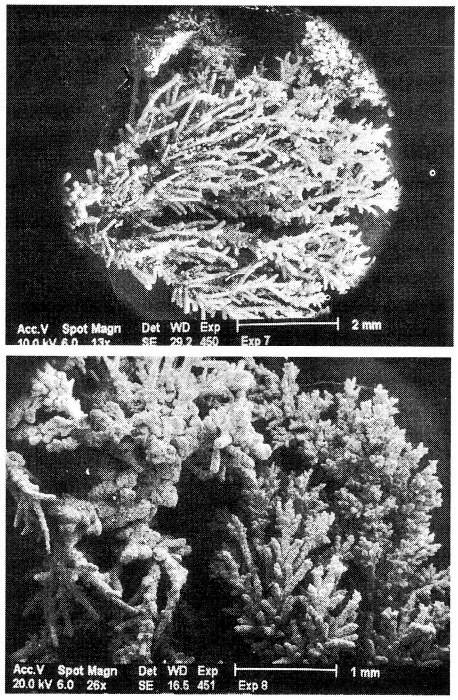

Figure 4c. *SEM observations on dendrites formation.*
Above: with 100 ml of cupric chloride solution
Below: with glycerine to cupric chloride ratio of 0.1

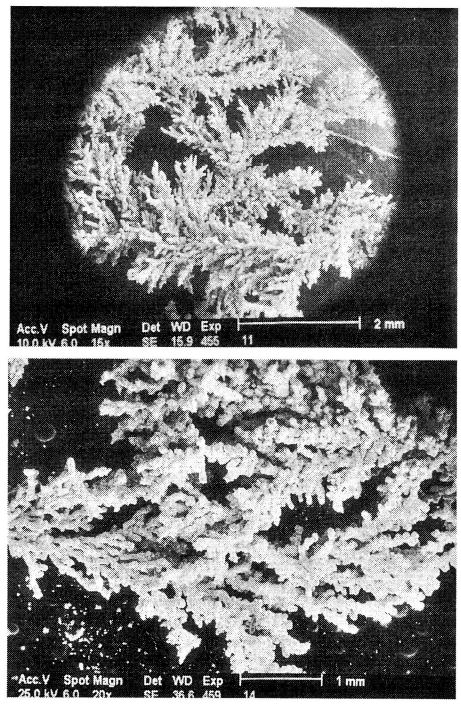

Figure 4d. *SEM observations on dendrites formation.*
Above: with glycerine to cupric chloride ratio of 1
Below: with glycerine to cupric chloride ratio of 10

Table 1. Weight percentages of particle size distribution

Trials number	Particle size distribution, S, in weight percentages		
	S < 45	45 < S < 180	S < 180
1 (no additives)	4.15	44.02	51.83
2 (10ml glycerine solution)	3.82	29.33	66.85
3 (50 ml glycerine solution)	0.85	13.81	85.34
4 (100ml glycerine solution)	6.12	27.06	66.82
5 (10ml cupric chloride solution)	9.23	23.63	67.14
6 (50ml cupric chloride solution)	1.75	4.71	93.54
7 (100ml cupric chloride solution)	10.59	14.82	74.59
8 (glycerine to cupric chloride ratio, r = 0.1)	1.67	5.51	92.82
9 (r=0.2)	3.08	7.08	89.84
10 (r=0.5)	3.34	5.06	91.60
11 (r=1.0)	3.08	14.95	81.97
12 (r=2.0)	3.46	19.27	77.27
13 (r=5.0)	11.56	64.03	24.21
14 (r=10.0)	3.61	15.54	80.85

Copper powder apparent density and flow rate

The commonly used indicators for characterizing the fluidity of powder in powder metallurgy context are powder apparent density and flow rate. Figure 5 shows the flake and nodular structures of the ball milled copper powders. It has a value of between 35 s/50 gm and 42 s/50 gm as indicated in Figure 6. Figure 7 exhibits the milled powder apparent density with different set of experimental conditions. The apparent density increases with an increasing ratio of glycerine to cupric chloride solution.

Figure 8 shows the variation of powder flow rate against the apparent density. A typical working powder characteristic lies in the region of rate between 30 to 40 s/50 g with an apparent density of 1.5 to 3.0 gcm^{-3}.

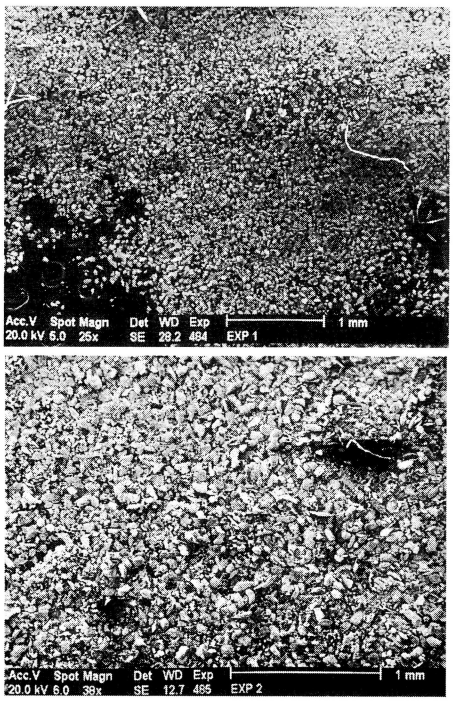

Figure 5. *SEM observations on flake and nodular structures of ball-milled powder.*
Above: without bath additives, 25X magnification
Below: with 10 ml of glycerine 38X magnification

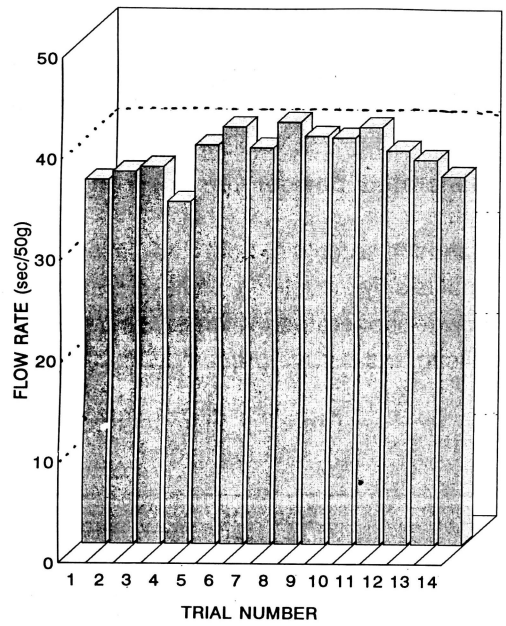

Figure 6. *Powder flow rate variation with different sets of experimental conditions.*

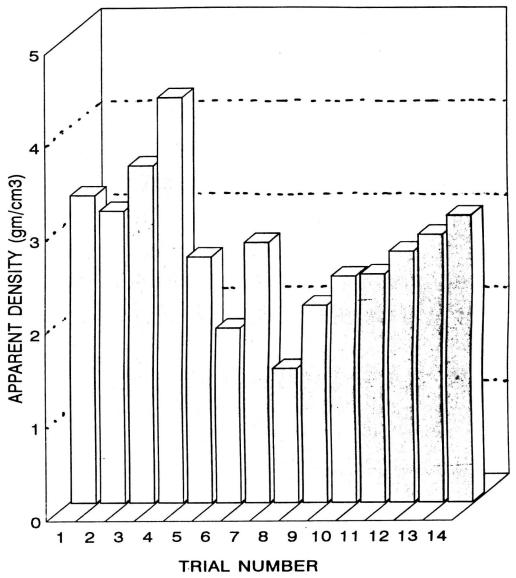

Figure 7. *Powder apparent density with different sets of experimental conditions.*

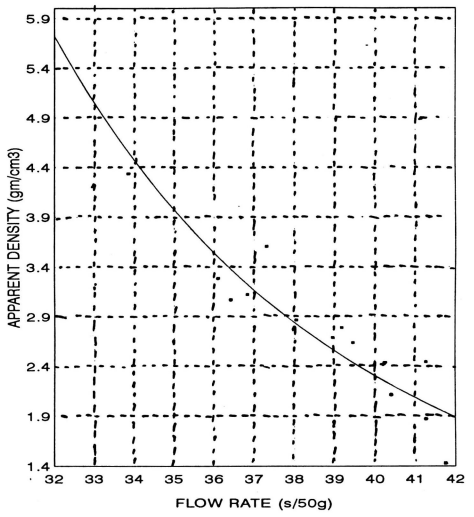

Figure 8. *Apparent density versus flow rate.*

Generated powder composition

Random sampling from four experiments were selected for elemental composition analysis by inductively coupled plasma technique. Table 2 illustrates the purity of copper powder generated, which exceeded 99 percent purity, with other elements such as zinc, silicon and carbon present as minor impurities.

Table 2. Elemental composition analysis by inductively coupled plasma technique

Elements present	Weight percent, wt %			
	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Copper	99.62	99.68	99.72	99.74
Zinc	0.28	0.29	0.28	0.28
Silicon	0.01	0.01	0.01	0.01
Carbon	0.015	0.014	0.014	0.032
Sulphur	0.002	0.002	0.041	0.096
Iron	0.003	0.003	0.005	0.007
Aluminium	0.006	0.005	0.004	0.004
Manganese	0.0008	0.0002	0.0002	0.0001

CONCLUSIONS

Both individual and combined effect of glycerine and cupric chloride added to the mother liquor increased the powder deposition rate. The additive added resulted in elongated and fine dendrites, in comparison to the powder generated without additives. Inductively coupled plasma analysis indicated that the copper powder purity exceeded 99.60 percent.

The milled copper particles have flake and nodular structures with a wide spectrum of particle size distribution, from less than 45 to greater than 180 μm. The particle flowability varied from 33.85 to 41.74 s/50 g and the apparent density varied from 1.430 to 4.333 gcm^{-3} which falls within the commercially available powder characteristics.

It is suggested that for comparison studies on the powder characteristics to be obtained, boric acid, glue and glucose be added as additives. Other suggestions include, the temperature effect, the anode-cathode surface area, anode-cathode distances and the effect of various type of input current signals. A study which involves other process parameters such as process economics and plant safety and maintenance could have been conducted through a pilot plant set-up. Other recommended powder characteristics which require in-depth studies are anodic polarization phenomena, powder compressibility and green strength.

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ACKNOWLEDGMENTS

The authors wish to thank all those involved in the project, particularly Dr. Mustaza Hj. Ahmadun for suggestions, encouragements and comments. The staff of Metals Technology Group SIRIM especially Mr. Mohd. Zahri Amat Sarbini and Mr. Ahmad Damanhuri Mahmud for operating the scanning electron microscope and in conducting the experiment. Finally, to Mr. Abdul Rahim Wasik, Chemical Testing Unit, SIRIM for conducting the inductively coupled plasma analysis.