

ELECTRODEPOSITION OF COPPER POWDER FROM COPPER SULPHATE SOLUTION IN PRESENCE OF GLYCEROL AND SULPHURIC ACID

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Abstract

Copper powder was obtained by electrodeposition of copper from glycerol and sulphuric acid. The morphology and particle size of these powders were studied. Dendritic, cubical, hexagonal and round shaped particles were obtained by electrodeposition from glycerol and sulphuric acid. Size of more than 85% particles was smaller than 60 μm . On the other side, size of powder particles obtained through XRD graphs and calculated applying Debye Sharer formula is in the range between 162 and 222 nm. The apparent density of copper powder decreased with increase in concentration of glycerol. The stability of the powder and current efficiency were also studied. It was found that in absence of copper sulphate there was some copper deposition on the cathode. The effect was discussed in present work. A new definition has been suggested for electrodeposition process.

Keywords: Electrodeposition, Copper, Stability, SEM, XRD, Particle size, Electrocatalytic and autodepositon

Introduction

Powder metallurgy method has many advantages. Powder can be produced from pure raw material with good characteristics and purity can be retained by controlling fabricating steps. This method involves cleaner and quieter operation with longer life of product. In certain applications powder metallurgy process has advantage over other methods. Conventional melting and other normal methods cannot produce powders of heavy metals which is only possible by powder metallurgy process.

Copper powder is used as alloying addition in production of refractory materials, fabrication of many industrial and machine parts such as clutch phasing, brake linings etc. Zheng and Jiang [1] reported the process of electrolytic production of copper

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powder by electrolysis of copper salt using high current density. Hou [2] studied structural and surface defects of electrodeposited copper powder by electrowinning process. Pattabhiraman *et al.* [3] presented briefly the electrolytic method of copper powder deposition from copper sulphate and chloride baths. Kokila *et al.* [4] developed a method of electroplating by copper from solution containing copper-sulphamate and copper-EDTA complexes. Delplancke *et al.* [5] have investigated the effect of high current density on electrowinning of copper. Juanma and Miguel [6] showed that the morphological patterns of copper powder, obtained from moderately concentrated copper solution, depend on current densities. Muresan *et al.* [7] worked on electrowinning of copper from different sulphate electrolytes. Borikar, Umare and Viswanath reported the effect of acetone on the electrowinning process for preparing copper [8], nickel [9], cadmium [10] and zinc [11] powders. Pricer *et al.* [12] investigated the influence of additive on electrodeposition. Recently, Viswanath and George reported preparation of cadmium [13] and copper [14] powders in sulphuric acid and glycerol medium.

In the present investigation, an attempt has been made to study the morphology and particle size of electrodeposited copper powder from glycerol and sulphuric acid where the glycerol percentage and current were varied. A method has been suggested for the determination of approximate density (apparent density) of copper powder. These densities may help to assess the nature and size of particles of the powder. The stability of electrodeposited copper powder was studied for its susceptibility to oxidation.

Experimental

Instruments

The bath solution (CuSO_4 , H_2SO_4 and glycerol) was placed into a single compartment of two-electrode cell. The electrodeposition experiments were performed using copper plate (13x2.3 x0.2 cm) as cathode and anode. Current was supplied by DC power supplier model 34 B DCPS (Testronix). All the experiments were carried out at $25 \pm 1^\circ\text{C}$. The temperature of the bath remained almost constant during the experiments. The current of 0.5, 1, 1.5 and 2 A was applied to the bath. The current variation was ± 0.01 A. The particle size analysis was performed on Saturn Digitizer II 5205 V1.01 and X-ray diffraction (XRD) analysis on Bruker AXSD8 Advance and morphological analysis were performed on scanning electron microscope (SEM) JEOL Model JSM - 6390LV operated at 1 pA to 1mA at Sophisticated Test and Instrumentation Center, Kochi, India.

Method of copper preparation

The concentration of glycerol was taken in volume percent and it was varied from 5 to 20%. The copper sulphate and sulfuric acid concentration were 0.2 N and 0.5 N, respectively, for all experiments. The total volume of the electrolytic bath solution was made up to 200 ml. Concentration of copper sulphate before and after experiment was estimated by titrating bath solution with 0.01 N sodium salt of Ethylenediaminetetraacetic acid (EDTA) using fast sulphon black-F (FSB-F) indicator. Volume of bath solution was measured after experiment. Duration time for deposition was 3 h to get sufficient quantity of powder for different types of analysis. The removal of the deposit from the cathode was performed in the distilled water by simple

scratching with glass rod. After washing with plenty of distilled water, the deposit was ground for about 30 min by adding 10 ml of distilled water. The copper powder was separated by decantation and filtration. The powder was dried in a hot air oven at about 90-100°C and stored in air tight bottle.

Results

Determination of apparent density of copper powder

The apparent density, d_a is given by the equation as:

$$d_a = d_w(W_3 - W_1) / (W_2 - W_1 + W_4 - W_3) \quad (1)$$

where: W_1 - the mass of dry empty density bottle, W_2 - mass of density bottle and distilled water;

W_3 - the mass of dry empty density bottle and copper powder (approximately from 1 to 1.5 g);

W_4 - the mass of density bottle with copper powder and distilled water;

d_w - the density of water at that temperature.

The apparent density of copper powder, obtained at different current levels and percent of glycerol is presented in Table 1. The apparent density may be expressed by the following equation:

$$d_a = (0.0684C - 0.229)C_g - 1.964 + 8.04 \quad (2)$$

where: C - current in amperes and C_g - percent glycerol.

Table 1. Apparent density of copper powder obtained at different Current and percent of glycerol

Current (A)	Percent of glycerol and Apparent density of copper (g/ml)				
	0%	5%	10%	15 %	20%
0.5	----	6.0	5.3	4.2	3.1
1.0	6.0	5.2	4.4	3.4	2.9
1.5	5.3	4.4	3.9	3.2	2.8
2.0	4.3	3.5	3.2	2.6	2.3

Cathodic current efficiency of electrodeposition (CED)

During the passage of one Faraday of current electrodeposition, electrowinning of copper and electrolysis of water occur. CED of copper was determined by mass loss of the copper anode. Our present studies also showed that copper anode was also dissolved due to electrocatalytic effect. Based on the current used for the particular period of electrolysis, the theoretically expected weight of copper deposition was calculated using Faraday's law:

$$W = Z I t \quad (3)$$

where: W , Z , I and t are theoretically expected mass of copper deposit, electrochemical equivalent of copper, current in A, time in s, respectively.

CED is calculated using the relation:

$$\text{CED} = (w / W) \times 100 \quad (4)$$

where: w - the mass of copper deposited on cathode during experiment. The data are presented in Table 2 A.

Table 2A. Cathodic current efficiency of copper deposition process obtained at different current and percent of glycerol

Current (A)	Percent of glycerol and CE of electro deposition of copper (%)				
	0%	5%	10%	15 %	20%
0.5	59.1	63.0	63.4	71.6	75.9
1.0	59.7	65.7	72.2	76.6	81.4
1.5	61.1	71.0	77.6	84.9	93.0
2.0	57.8	66.5	75.9	82.6	89.3

The current efficiency of electrodeposition may be expressed by the following formula:

$$\text{CED} = (-0.86C^3 + 3.012C^2 - 2.523C + 1.46) C_g - (2.6C^2 - 6.5C - 56.4) \quad (5)$$

where: C - current in A and C_g is percent glycerol.

Reaction mechanism of electrodeposition of copper

Copper dissolves at anode to give copper ions. These copper ions discharge at cathode to give copper metal.

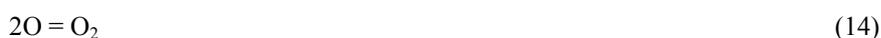
Reaction at anode:



Reaction at cathode:



The important electrode reactions during the electrowinning process were discussed by Viswanath and George [14]. The increase in the acid concentration is not only due to formation of sulphuric acid but is also due to organic acids formed due to oxidation of glycerol.



Oxidation of glycerol

While liberated oxygen at anode reacts with glycerol and forms several products. These reactions are discussed by Viswanath and George [14]. The formed product contains different organic acids like glyceric acid, tartonic acid and mesoxalic acid which cause to increase the acid.

Cathodic current efficiency of electrowinning (CEE)

Few solutions are analyzed for copper quantity after the experiment. It was found that Cu^{++} ion concentration was decreased. CEE may be expressed by the equations 3 and 4. The data are presented in Table 2B.

Table 2B. Cathodic current efficiency of electrowinning process obtained at different current and percent of glycerol

Current (A)	Percent of glycerol and CE of electrowinning of copper (%)				
	0%	5%	10%	15 %	20%
0.5	5.6	5.9	13.0	---	---
1.0	5.5	---	9.1	11.7	---
1.5	4.5	6.4	---	7.4	---
2.0	4.4	---	5.7	6.7	7.8

CEE and autodeposition studies

It was observed that in absence of copper sulphate, and under similar conditions there is some copper deposited on cathode and anode lost some mass. At the same time, almost black-reddish shade loose powder deposit was found on the anode. This type of black-reddish powder is not found on the anode in the original experiments. This powder was removed by scratching and analyzed. If the anode was left for some time in the solution, the anode powder turned into hard layer and could not be removed by simple scratching. The powder was found to be copper metal. The solution turned into blue. If acid concentration is kept at 0.05N the black-reddish powder was found on the anode along with small blue powder. The solution turned blue and blue precipitate was found in solution which settled later at the bottom of the cell. If sufficient acid is not present but glycerol is present in the solution, no precipitate is found. When similar experiment was carried in 0.1N ammonium hydroxide a large amount of blue precipitate was observed and the solution was colorless. The blue precipitate was found to be copper hydroxide $\text{Cu}(\text{OH})_2$. The hydroxyl ions obtained from dissociation of water attack the positively charged copper anode and form copper hydroxide which in turn reacts with acid and forms copper sulphate. This copper sulphate solution acts as medium for electrodeposition and electrowinning. The current efficiency of electrocatalytic reaction may be expressed by the above equations (3 and 4). Here, w is the mass loss of the copper anode during experiment and the relative mass of anode is given by the expression, as:

$$\frac{\text{Mass loss of anode in absence of electrolyte}}{\text{Mass loss of anode in presence of electrolyte}} \quad (15)$$

The data are presented in Table 2C.

Table 2C. Cathodic current efficiency of electrocatalytic and autodeposition process obtained at different current and percent of glycerol

Current A	Percent of glycerol and CE of electrocatalytic process				
	Relative mass of anode				
	0%	5%	10%	15 %	20%
0.5	99.1	98.9	98.1	98.6	98.0
	0.99	0.98	1.21	1.04	1.08
1.0	101.6	100.9	99.9	96.0	97.5
	1.31	1.11	1.06	1.11	0.86

Mathematical concept of combined study of electrocatalytic and electrowinning

The electrocatalytic and electrowinning are combined processes occurring simultaneously during electrodeposition of metals. The result is either increase or decrease in the concentration of electrolyte or metal ions in the solution. The difference between initial concentration (C_i) and final concentration (C_f) of electrolyte is Δc . Δc is a function of applied current (I), glycerol percent (C_g), initial concentration (C_i), time (t) and acid concentration (C_a). If C_i and t are maintained constant and sufficient acid is available, then Δc is a function of I and C_g , as:

$$\Delta c = f(I, C_g) \quad (16)$$

Differentiating the equation 16:

$$d(\Delta c) = (\delta(\Delta c) / \delta I)_{C_g} dI + (\delta(\Delta c) / \delta C_g)_I dC \quad (17)$$

where: $(\delta(\Delta c) / \delta I)_{C_g}$ and $(\delta(\Delta c) / \delta C_g)_I$ are partial derivatives.

If C_g is kept constant, then the second term is equal to zero and above equation may be written as complete derivative:

$$d(\Delta c) / dI = (\delta(\Delta c) / \delta I)_{C_g} \quad (18)$$

Δc may be expressed in power series of I as a polynomial:

$$\Delta c = a_1 I^x + a_2 I^{x-1} + \dots \quad (19)$$

where: a_1, a_2 etc are coefficients of the polynomial and $x, x-1$, are indices of the polynomial.

This polynomial is differentiated with respect to I and derivative $d(\Delta c) / dI$ is calculated. This derivative is function of Δc and may be written as:

$$d(\Delta c) / dI = k(\Delta c)^n \quad (20)$$

where: k is the constant of process similar to specific reaction rate constant and n is order of process. The logarithmic expression for the equation may be expressed as:

$$\ln[d(\Delta c) / dI] = n \ln[(\Delta c)] + \ln(k) \quad (21)$$

The plot of $\ln[d(\Delta c)/dI]$ vs. $\ln[(\Delta c)]$ gives a straight line. n is slope and $\ln(k)$ is intercept of the line. The values of n and $\ln(k)$ are presented in the Table 2D. The unit of k is mass (g) of CuSO_4 per current (A) or g of Cu per A or equivalents CuSO_4 per Faraday or equivalents Cu per Faraday. When glycerol percent is zero the order of process is zero which indicates the process is independent of electrolyte concentration. n and $\ln(k)$ are expressed by following equations:

$$n = -0.0824C_g + 1.4663 \text{ and } \ln(k) = -0.0065C_g^2 + 0.0981C_g - 1.4092 \quad (22)$$

These equations are valid when the glycerol percent varies from 5 to 20.

When Δc is constant the term $d(\Delta c)/dI$ becomes zero. This is known as inflection point of the curve. I and Δc values of the inflection point are also presented in Table 2D. At this point, rate of electrowinning and rate of electrocatalytic process are equal or of electrodisolution of copper is equal to removal of copper ions from the solution. The mass loss of copper anode (Cu_g) may be related to current (C) and glycerol percent (C_g) by the following equation:

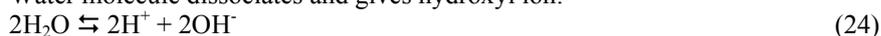
$$\text{Cu}_g = (0.0724C_g + 2.2014) + 0.0016C_g^2 - 0.0607C_g + 0.6043 \quad (23)$$

Table 2D. The constants for the combined process of electrocatalytic and electrowinning

% of glycerol	n	$\ln(k)$ g of Cu A ⁻¹	Inflection point values	
			I(A)	$\Delta c(\text{g Cu})$
0	0.000	-1.632	---	---
5	1.050	-1.070	0.536	0.221
10	0.633	-1.119	0.562	0.249
15	0.259	-1.371	0.615	0.345
20	-0.191	-2.073	1.340	0.533

Reaction mechanism of electrocatalytic effect and autodeposition of copper

Water molecule dissociates and gives hydroxyl ion:



This hydroxyl ion reacts with copper anode and forms copper hydroxide:



The formed copper hydroxide reacts with sulphuric acid and copper sulphate is formed:



If the acid concentration is less and sufficient glycerol is present in the solution, no precipitate is found because the copper hydroxide reacts with the organic acids like glyceric acid, tartonic acid and mesoxalic acid, which are formed due the oxidation of glycerol by the nascent oxygen liberated at anode, forming respective copper salt of organic acid.

Determination of stability of copper powder

Copper powder is stored for around fifty days in an air tight sealed bottle then it is studied for its stability. Accurately weighed (0.7 ± 0.3) gram of copper powder was taken in 100 ml 0.5 N H_2SO_4 . The solution is stirred with a magnetic stirrer for one hour. The solution is filtered and the dissolved copper in the filtrate was estimated by titrating the filtrate against standard EDTA (0.01 N) using FSB-F indicator. Copper powder is susceptible to oxidation and forms copper oxide (CuO). This oxide reacts with sulphuric acid and forms copper sulphate. However, copper does not react with sulfuric acid. The oxidative stability (OS) of copper was estimated using the expression:

$$\frac{\text{Weight of metal powder undissolved}}{\text{Weight metal powder taken}} \times 100 \quad (27)$$

The data are presented in Table 3. The oxidative stability may be expressed by the following equation:

$$OS = (0.3816C^3 - 1.7184C^2 + 2.5406C - 0.0924)C_g - (3.7333C^3 - 14.4C^2 + 14.267C - 75.1) \quad (28)$$

where: C is current in A and C_g is percent glycerol.

Table 3. Oxidative stability of copper powder obtained at different current and percent of glycerol

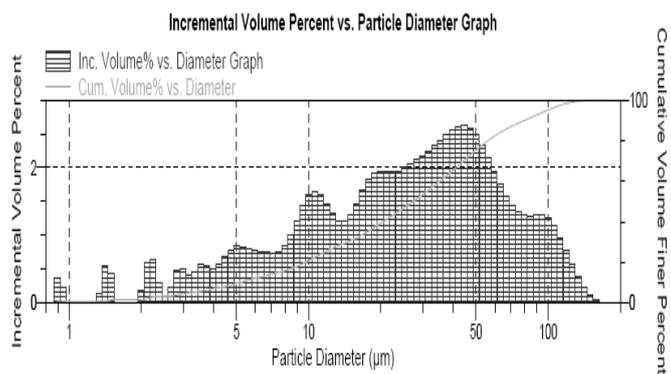
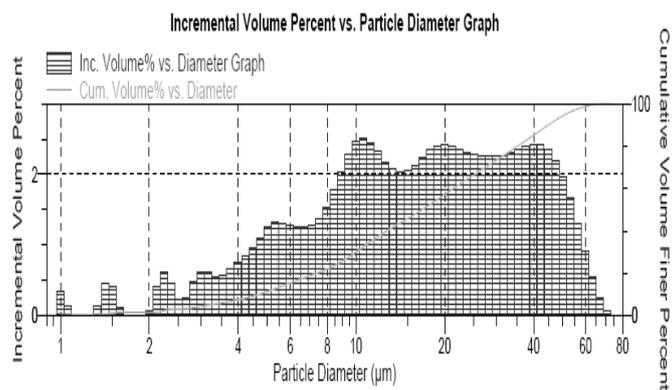
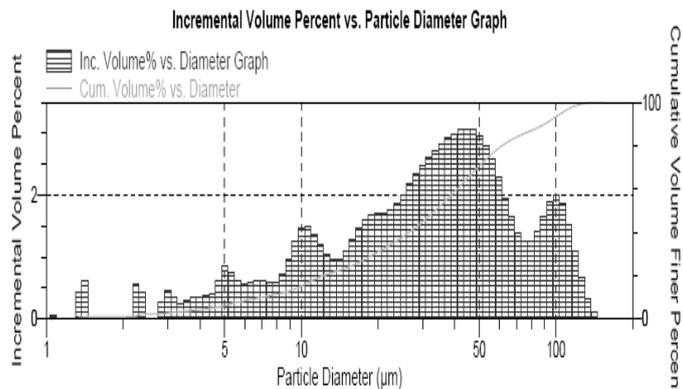
Current (A)	Percent of glycerol and oxidative stability of copper(%)				
	0%	5%	10%	15 %	20%
0.5	70.7	75.0	80.0	83.0	86.6
1.0	72.1	76.3	82.4	89.0	93.6
1.5	73.5	79.5	84.6	90.4	96.8
2.0	74.4	80.0	86.1	92.1	97.6

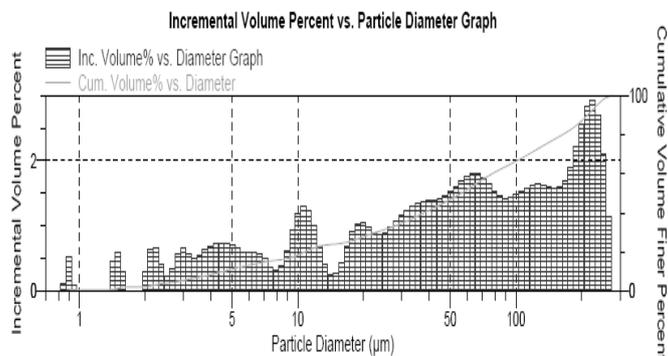
Particle size analysis

Prepared copper powder particle size was analyzed by two methods, *i.e.* particle size distribution curve analysis and XRD –Debye Sharer formula calculations.

Particle size distribution

The distribution of copper particle size is shown in Fig.1 and the data of distribution are given in Table 4. Sulfuric acid 0.5 N and 15% glycerol medium with 1 A current give satisfactory small particle size. More than 85% particle was below 60 μm . 20% glycerol with 0.5 A current also gives desirable smaller particle size and shows some nano-character. This is evident from SEM and XRD studies also.





(d)

Fig. 1 Particle distribution (a) 20% glycerol & 0.5 A; (b) 15% glycerol & 1 A; (c) 15 % glycerol & 1.5 A and (d) 5% glycerol & 2 A.

Table 4. particle size of copper powder obtained at different current and percent of glycerol

Current & % of glycerol	Percent of particles						
	1-15	15-30	30-45	45-60	60-75	75-85	85-100
	Size of particles in μm						
0.5 A & 20	1.433	9.926	19.373	29.998	40.880	54.546	72.945
	9.926	19.373	29.998	40.880	54.546	72.945	123.198
1.0 A & 15	1.440	5.863	10.003	14.627	21.360	31.135	39.781
	5.863	10.003	14.627	21.360	31.135	39.781	60.868
1.5 A & 15	1.417	7.426	14.485	23.682	35.363	49.595	65.204
	7.426	14.485	23.682	35.363	49.595	65.204	126.793
2A & 5	1.427	7.048	22.634	46.462	77.792	136.550	190.588
	7.048	22.634	46.462	77.792	136.550	190.588	260.173

XRD studies of particle size

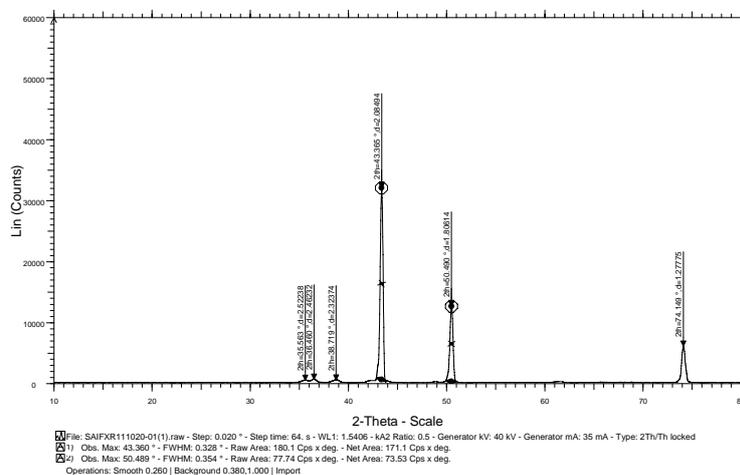
The particle size is calculated from XRD data of peaks from graph and by using Debye-Sharer formula:

$$D = k \lambda / \beta \cos \theta \quad (29)$$

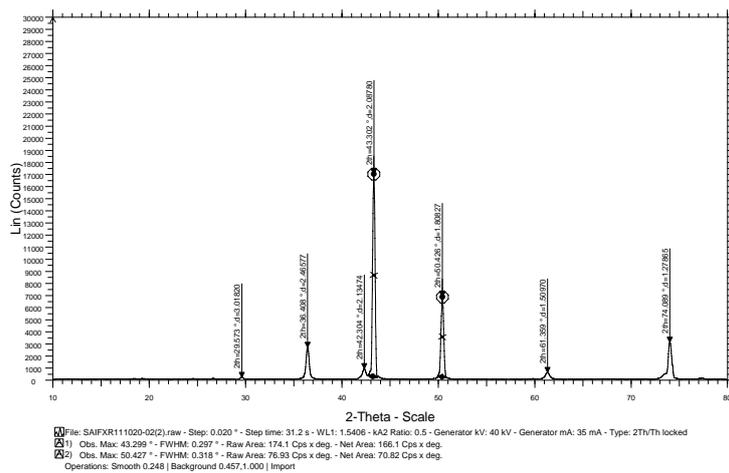
where: k - crystalline shape factor and λ - wave length in angstrom (Å)

$$\beta \text{ (radian)} = \text{FWHM} \times \pi / 180 \quad (30)$$

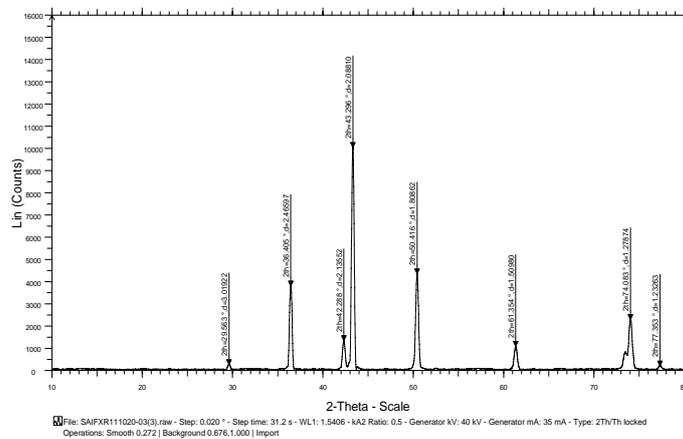
where: Full-Width Half-Maximum (FWHM) - from instrument data, π is 22.7 and θ is angle. Particle size is shown in Table 5. XRD pattern of copper powder particles of some samples are shown in Fig.2. A peak shows 2θ values and is related grain size of the particle in nm. The height of the peak indicates intensity of diffraction or may be related to number of particles.



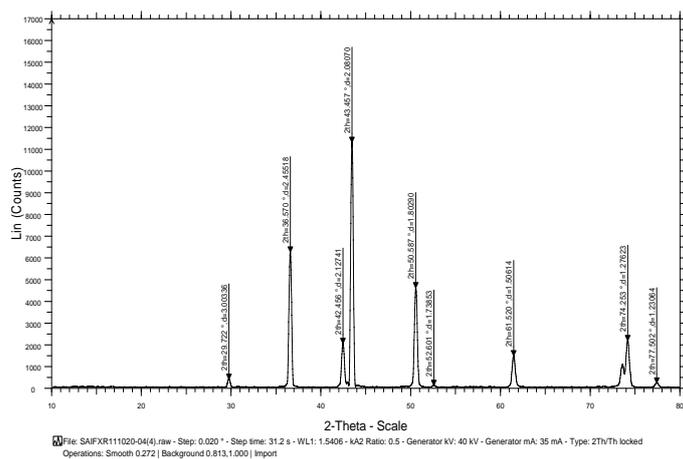
(a)



(b)



(c)



(d)

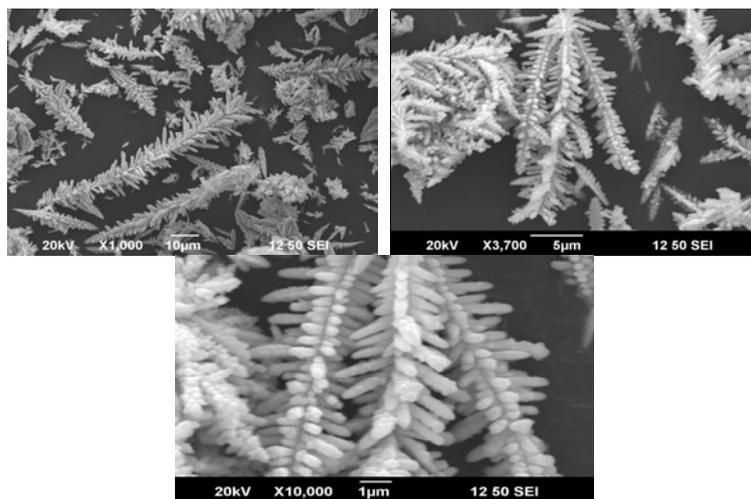
Fig. 2 XRD Pattern of copper powder particles (a) 20% glycerol & 0.5A; (b) 15% glycerol & 1 A; (c) 15% glycerol & 1.5A; (d) 5% glycerol & 2 A

Table 5. Particle size of copper powder obtained at different current and percent of glycerol

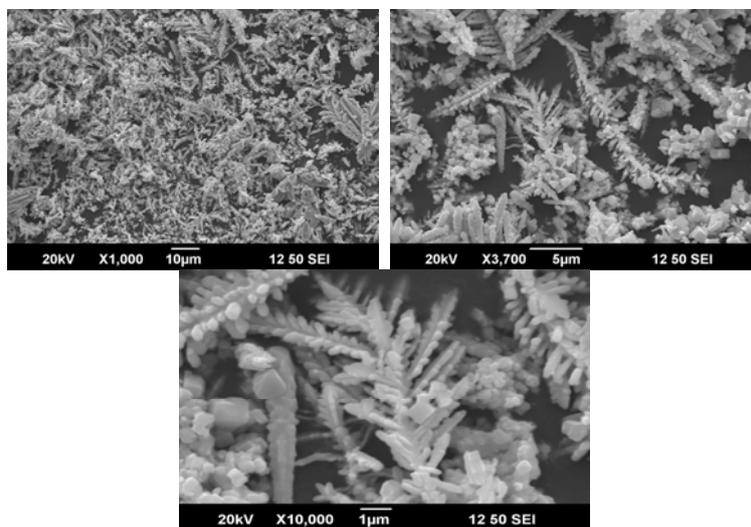
Current & Percent of glycerol	Particle size in nm
0.5 A & 20%	191.1, 200
1 A & 15%	213.9, 222.1
1.5 A & 15%	192, 213.9
2 A & 5%	162.3, 191.1

Morphological studies

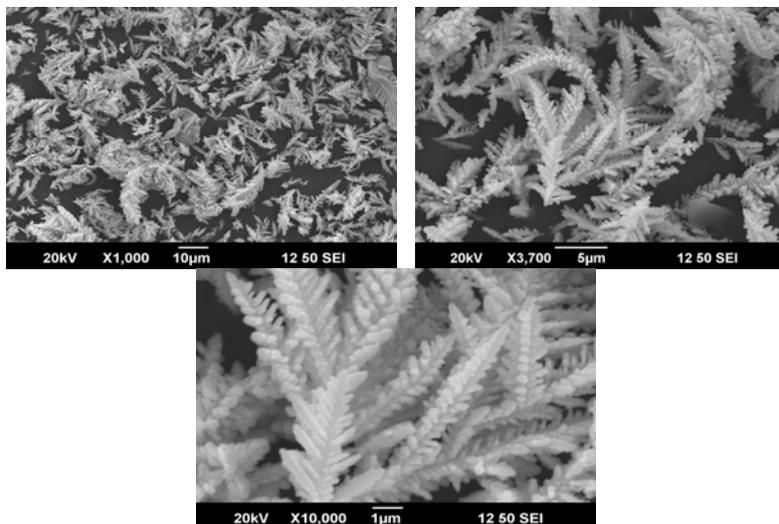
SEM microphotographs of copper powder are shown in Fig.3. The relevant physical data of respective powders are presented in Table 6. These results indicate that the lower is the apparent density smaller is the particle size of electrodeposited powder.



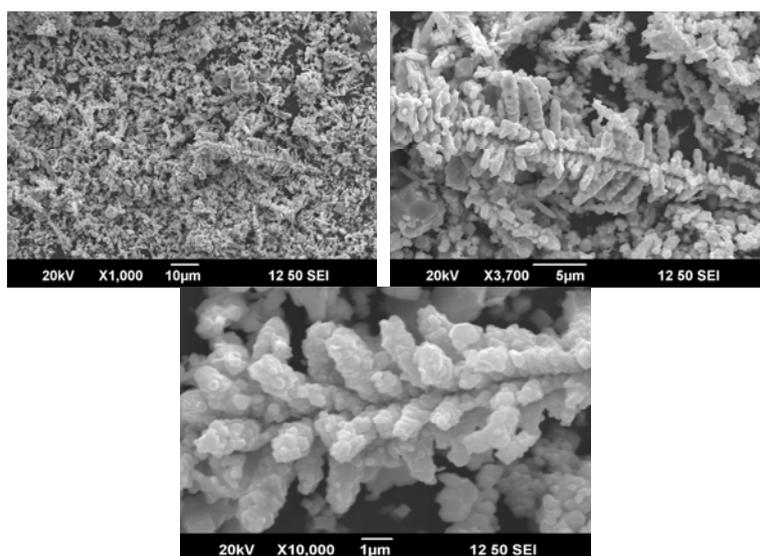
(a)



(b)



(c)



(d)

Fig.3-SEM microphotographs of copper powder (a) 20% glycerol & 0.5A; (b) 15%glycerol & 1A; (c) 15 % glycerol & 1.5 A and (d) 5% glycerol & 2 A

Table 6. Morphology of copper powders and related data

Current (A) Percent of glycerol	Apparent density	Stability	Morphology of the powder and percentage particle size below 100 μm
0.5 A & 20%	3.1	86.6	Dendrites with longer branches, 85%
1.0 A & 15%	3.4	89.0	Almost cubicle square dendrites, hexagonal, 100%
1.5 A & 15%	3.2	90.4	Dendrites with cube and long branches, 85%
2.0 A & 5%	3.5	80.0	Dendrites, bonded spherical, 65%

Discussion

The apparent density of the powder decreases with increasing percent of glycerol and current. The formation of dendrites powders is decreased by increase of percent of glycerol and current. Therefore, the decrease in apparent density may be considered as a measure of decrease of dendrites. The percent of glycerol between 10 and 15 % and current from 1 to 1.5 A produce powders which contain more of square, cubical, hexagonal particles and less weakly bonded dendrites particles.

When the electrodeposition process was completed the acid concentration increased. This increase of the acid concentration is due to formation of sulphuric acid from sulphate ions and different carboxylic acid by the electrolytic oxidation of glycerol molecules and elimination of water molecules from the solution by electrolysis. The increase in the acid concentration was found to be in the range from 0.12 to 0.15N.

During electrolysis Cu anode dissolves into solution, all positive ions align and migrate towards the cathode, while negative ions migrate towards the anode. The metal ion is discharged at the cathode. The solid metal atoms are deposited on the cathode should have strong metallic bond. A large amount of hydrogen liberated at the cathode makes the deposit porous. The solution containing organic solvent which is covalent in nature also disturbs this ion environment particularly at the cathode causing loose bonding between metal-metal atoms. The effect of these parameters results in the formation of metallic powders.

It was found that increase in the percent of glycerol and current in the solution increases oxidative stability of powder. If the powder has large surface area, lesser is its oxidative stability. This may be due to the fact that more number of copper atoms at the surface has free valences. In the present case oxidative stability of powder is due to smaller size of the particles having small surface area.

In all cases the particle size analysis shows that 85% of particles are smaller than 73 μm , whereas 75% of particles are smaller than 55 μm . During the passage of 1 A current through 15% glycerol the size of all particles is less than 61 μm and oxidative stability of powder is around 90%. Moreover this electrodeposition method produces particles of lower size than the electrowinning method. XRD studies indicate that at higher current the amount of nano-particles increases. However, low glycerol percent produces particles of larger size particles as evident from Table 4 (2A and 5% glycerol).

The current efficiency of electrocatalytic and autodeposition (Table 2C) suggests that the reaction does not follow the Faraday's law as it is almost 100% or sometime more than 100%. Because of this reason and also because of the electrically charged copper anode these reactions (eqs 24-26) are occurring. These reactions may be

regarded as electrocatalytic reactions. The relative mass studies indicate that in number of cases anode dissolution is higher in the absence of electrolyte solutions than in the presence of electrolyte solution. After some copper sulphate is formed the electrodeposition takes place. Hence, this reaction may be called autodeposition.

The electrocatalytic dissolution of anode is zero order process (eq.23) and also a spontaneous one. If sufficient acid is available in the solution the anode metal dissolves and gives corresponding acid salt (eqs.23-26) otherwise hydroxide is formed (eqs.23&24). Electro winning occurs under specific conditions and inert metal like platinum acts anode. Under same conditions the electrodeposition occurs too. Electrodeposition is neither an independent nor an unique individual process. Therefore, electrodeposition may be defined as a combination of electrodisolution of anode metal by electrocatalytic effect and electrowinning process. When electrowinning is faster than electrodisolution then concentration of electrolyte decreases in the solution, otherwise the concentration of electrolyte increases in the solution. This fact is noticed by the authors in the study of electrodeposition of some other metal.

Conclusions

It may be concluded that 15 % glycerol and 1-1.5 A current give powder having lower particle size and high oxidative stability. Under these conditions, the size of 85% particles is smaller than 61 μm and powders are free from dendrites and stability is around 90%. This electrocatalytic and autodeposition studies indicate that electrodeposition is a very complex process. This electrocatalytic effect may be helpful in preparation of salts particularly metal salts of organic acids. A new definition is given to electrodeposition process.

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