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## Preparation of copper powder by glycerol process

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### Abstract

A simple, least energy intensive, efficient, low temperature chemical process for the production of copper powder of narrow size distribution is described. It involves reduction of copper salts by glycerol under atmospheric conditions at a temperature below 240°C. The powders produced by this process have been characterized by X-ray diffraction, chemical composition, BET surface area analysis and scanning electron microscopy. The powder is well crystalline and contains oxygen, carbon, and hydrogen as impurity elements. The purity of the powder produced by the process depends on the starting compound of copper. The glycerol process using copper acetate as starting compound yields copper powder having a purity of 99.7%. © 2002 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

Conductive pastes have been used for the formation of thick film conductors such as electrodes or conductive patterns in multilayered electronic parts and printed circuit boards. Conductive paste includes metal powder dispersed in an organic vehicle along with glass frit. Replacement of precious metal powders like gold, silver or palladium by copper powder for production of conductive paste for hybrid integrated circuit and for the metallization of multilayer ceramic capacitor (MLCC) is a current trend in the electronic industry. Copper offers several economic and

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performance advantages over precious metals. The conductivity of copper is as good as silver and 40% better than that of gold. The stability of copper at high frequencies is better than gold or silver and it is compatible with most solder materials [1].

For conductive paste application, it is required to use high purity crystalline non-agglomerated copper powder, which is free from surface oxidation. The oxidation of the powder leads to the formation of a thick film conductor with bad appearance and poor solderability. In addition to the purity, it is highly desirable that the particles should have narrow size distribution in order to precisely control the thickness of the electrode formed with the conductive paste and also facilitate intimate metal bonding [2].

Reduction of metallic compounds by gases is a widely employed method of producing metal powders. Gases such as hydrogen, dissociated ammonia, carbon monoxide, partially combusted hydrocarbon are few of the examples of the reducing agents used. Copper powder can be produced by atomization, electrolysis, reduction of sulfate solution using hydrogen and by solid-state reduction. Each of these processes, however, produces particles of varying physical properties. Among the various methods of preparation of copper powders, chemical routes facilitate molecular/atomic level controls and also efficient scale up for processing and production [3]. Precipitation of metallic copper is accomplished through chemical reduction of a salt, oxide, or hydroxide of copper in solution. Various reducing agents like starch [4], hydrazine [5], hydroxylamine hydrochloride [6] etc. have been used for the production of copper powder.

One of the successful methods for preparation of metal powders belonging to groups VIII and IB is the so-called polyol process [7]. The polyol process essentially involves preparation of metal powders by heating a suitable inorganic/organic metallic salt in a polyol, which acts as a solvent as well as a reducing agent.

In the polyol process metal particles are formed through nucleation and growth steps from the solution. The synthesis of metal powders of well-defined particle shape and size with controlled size distribution is facilitated by the kinetic control of the nucleation and growth steps. Definite separation between the nucleation and the growth stages is a prerequisite for the formation of mono-size particles [7]. One of the measures to separate growth from nucleation may be addition of seed particles where seed crystals act as foreign nuclei and homogeneous nucleation is thereby replaced by heterogeneous nucleation.

Fievet et al. [7] has described a process for preparation of metal powder using ethylene glycol/diethylene glycol as a polyol. In the present study, a process for preparation of copper powder having narrow size distribution is described using glycerol. Glycerol is having higher boiling point and dielectric constant compared to other polyols (Table 1). Due to its higher boiling point, it can provide higher reaction temperature at atmospheric pressure. Due to the presence of one secondary and two primary alcoholic groups in its structure, glycerol can reduce salts of easily reducible metals. Though ethylene glycol, diethylene glycol, or their mixtures have been studied for preparation of metal powders, the use of glycerol to prepare metal powders has not been investigated.

Table 1

Boiling point and dielectric constant (at 25°C) of different alcohols at one atmospheric pressure [8]

Alcohol	Boiling point (°C)	Dielectric constant ( $\epsilon$ )
Methanol	64.7	32.70
Ethanol	78.3	24.55
2-Propanol	82.3	19.92
Isobutyl alcohol	107.7	17.93
Ethylene glycol	197.3	37.70
Glycerol	290.0	42.50

## 2. Experimental

For the preparation of copper powder three salts were selected. These were AR grade copper oxide, copper hydroxide, and copper acetate. A predetermined amount of starting salt was suspended in glycerol (AR grade). The molar ratio ( $R$ ) between starting metal compound and glycerol was fixed at 0.02. The suspension was heated, while stirring, by using a hot plate. The copper salts started to dissolve with increase in temperature. The reaction temperature was measured using a thermometer inserted in a glass port that was submerged in the solution.

The suspension of copper powders obtained was cooled down to room temperature and then diluted with ethanol. The precipitated metal powders were separated from the solution by repeated centrifugation using ethanol as a washing agent. The washed powder was dried under vacuum at 80°C for 2 h.

Powder samples were characterized by X-ray diffraction (XRD, Philips Analytical, Model PW1710) using Cu K $\alpha$  radiation at a scan rate of 0.05°/s. The powder morphology was studied by scanning electron microscope (SEM, Cambridge, Stereoscan-240, UK). Specific surface area measurement of the powders was carried out by using nitrogen adsorption BET surface area analyzer (CE Sorptomatic 1990). Before carrying out the surface area analysis the powder samples were thoroughly dried under vacuum at 400°C for 2 h to remove any glycerol or its oxidation product from the surface of the powder particles.

## 3. Results and discussion

The basis of selection of metal precursor salts for the preparation of copper powder lies in the fact that it should be dissolved and reduced to metal by glycerol at the reaction temperature and form by-product that would not add any impurity to the powder. Though the solubility of the copper precursor compounds in glycerol is low at room temperature, it increases with temperature leading to a transparent colored solution, color of the solution being dependent on the starting precursor. Complete dissolution of the copper precursors takes place before reduction by glycerol. The metal particles form by homogeneous nucleation and growth mechanism. The morphology of the metal powders produced through this route can be manipulated by heterogeneous

nucleation by adding nucleating agents such as palladium powder. In the present study, no external nucleating agents have been incorporated in the suspension.

When copper oxide is used as the precursor compound, the precipitation of copper from the solution starts at a temperature of 210°C and completes at 220°C, which is lower than the boiling point of glycerol. In the case of preparation of copper powder from hydroxide, the precipitation completes at 230°C. The copper powder precipitates at a temperature of 234°C when acetate salt is used. The total incubation period for the precipitation of metal powder is less than an hour, which is much less than other polyol processes as described by Chow et al. [3].

The XRD patterns of the copper powders prepared through glycerol route are shown in Figs. 1–3. The pattern of the three powders corresponds to the FCC copper phase. The powders are well crystallized as evidenced by the XRD pattern. The broadening of peaks of the pattern correlates to the fineness of the copper particle. The crystallite size of the powder was calculated by line broadening of (1 1 1) peak of XRD pattern using Scherrer's formula

$$\text{Crystallite size} = \frac{0.9\lambda}{\beta \cos \theta}$$

where  $\beta$  is the broadening due to the crystallite size which is obtained after correcting the measured value ( $B$ ) with instrumental broadening ( $b$ ) as per the formula:  $\beta^2 = B^2 - b^2$ . The instrumental broadening was measured using silicon as standard.

The BET surface area of the powders produced through glycerol route is shown in Table 2. With the assumption of monodispersed spherical shaped crystal particles, the particle size ( $\mu\text{m}$ ) was calculated based on the relation

$$\text{Particle size} = \frac{6}{\rho S_{\text{BET}}}$$

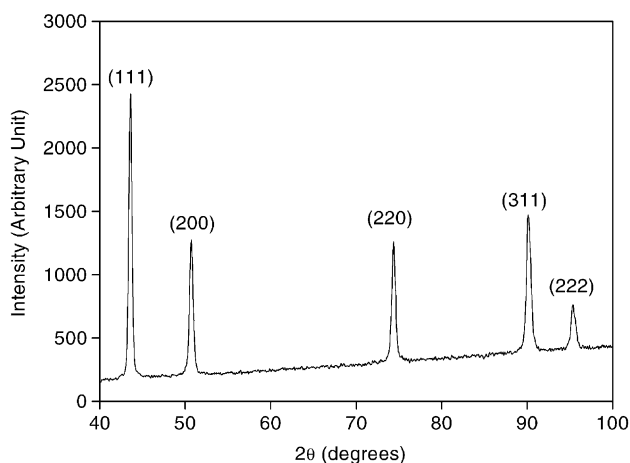


Fig. 1. XRD pattern of copper powder produced through glycerol route using copper oxide as precursor.

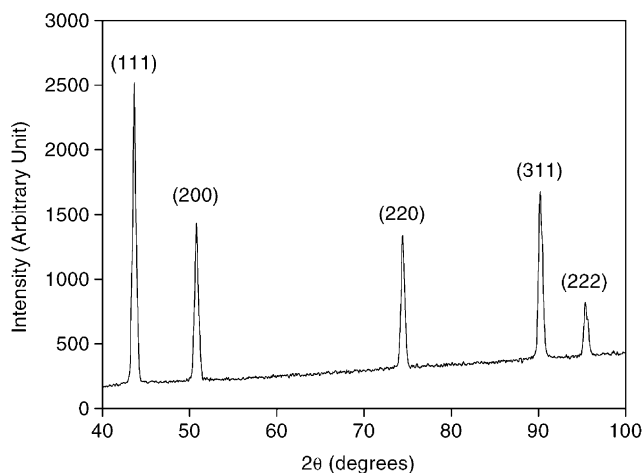


Fig. 2. XRD pattern of copper powder produced through glycerol route using copper hydroxide as precursor.

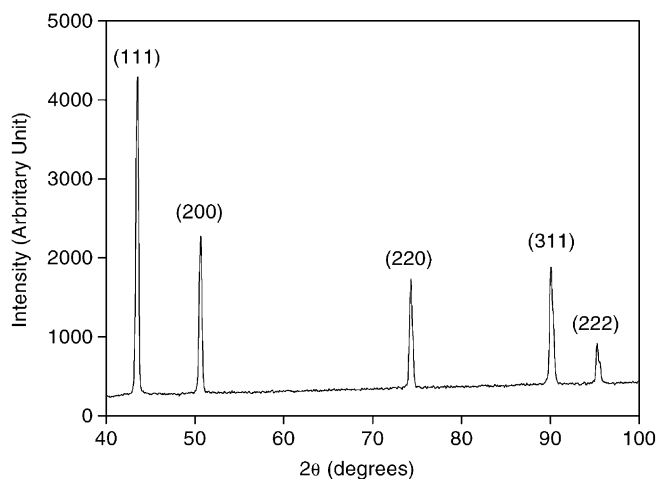


Fig. 3. XRD pattern of copper powder produced through glycerol route using copper acetate as precursor.

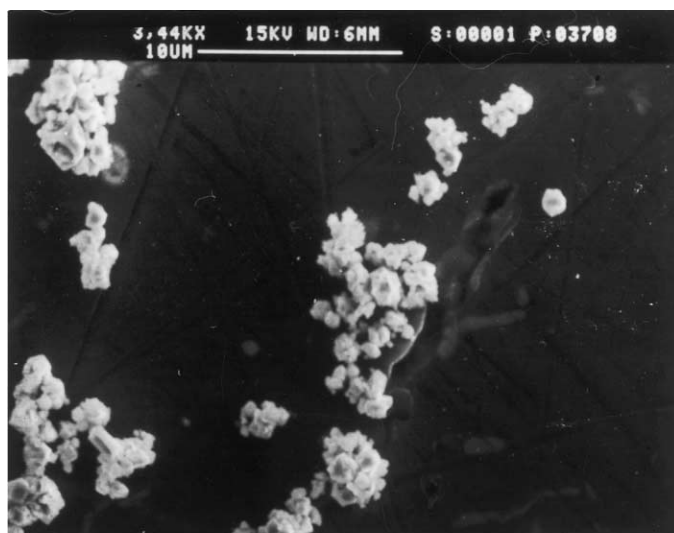
Table 2

BET surface area measurement and calculated crystallite size of copper powders produced through glycerol process

Copper compound	BET specific surface area ( $S_{\text{BET}}$ ) ( $\text{m}^2/\text{g}$ )	Calculated particle size from $S_{\text{BET}}$ (nm)	Calculated crystallite size from XRD (nm)
Oxide	5.48	123	71
Hydroxide	9.56	70	53
Acetate	3.70	182	105

where  $\rho$  is density of copper ( $\text{g/cm}^3$ ) and  $S_{\text{BET}}$  is the measured value of specific surface area in  $\text{m}^2/\text{g}$ . The crystallite sizes of copper powders as calculated from specific surface area data as shown in Table 2 reveal the potential of glycerol process to produce nanostructured copper powder.

The SEM photomicrographs of the copper powders produced from copper oxide are shown in Fig. 4a and b. The micrographs reveal that the powder is made up of particles of narrow size distribution having an average particle size of  $1\ \mu\text{m}$ .

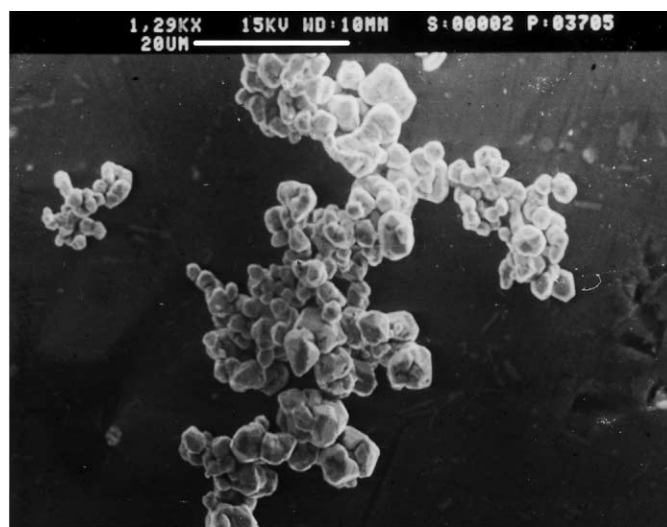


(a)



(b)

Fig. 4. (a) and (b) SEM photomicrographs of the copper powder produced through glycerol route from copper oxide as precursor.



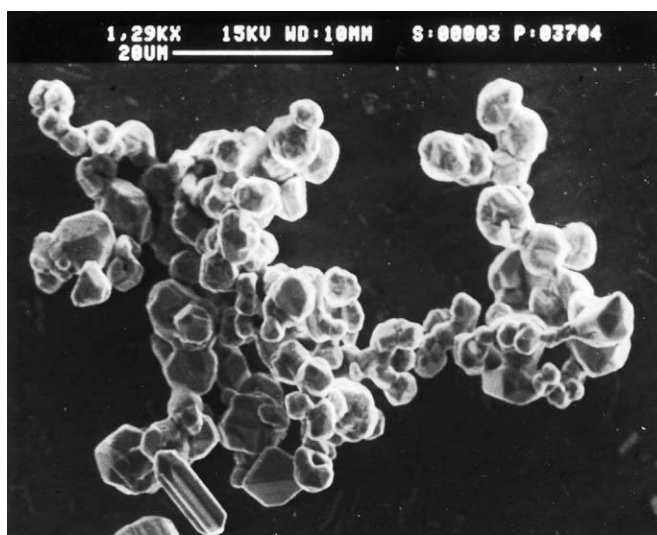
(a)



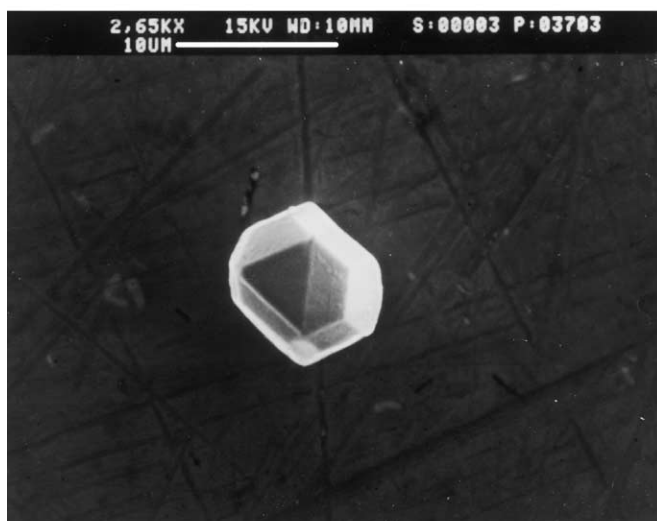
(b)

Fig. 5. (a) and (b) SEM photomicrographs of the copper powder produced through glycerol route using copper hydroxide as precursor.

Fig. 5a and b show, the photomicrographs of the copper powder produced through glycerol route using copper hydroxide as starting material. The powder is spheroidal having narrow size distribution. The average particle size of the powder is  $3.5\ \mu\text{m}$ . The SEM photomicrographs of the copper powder produced from copper acetate reveal that the powder is made up of spheroidal particles with a faceted structure (Fig. 6a and b). The powder produced from copper acetate as precursor salt comprises of particles of narrow size distribution having an average particle size of  $5.6\ \mu\text{m}$ .



(a)



(b)

Fig. 6. (a) and (b) SEM photomicrographs of the copper powder produced through glycerol route from copper acetate as precursor.

The above results suggest that dense, polycrystalline copper powder with narrow size distribution is produced through glycerol route. For a given molar ratio ( $R$ ), the average particle size as well as crystallite size of the powder depends on the type of copper precursor used. The particle size of the powders produced from different precursors, as calculated from  $S_{\text{BET}}$  data are higher than the respective crystallite size obtained from X-ray line broadening. However, these calculated particle sizes are lower as compared to the particle sizes estimated from SEM observations. The particle size of the powder is calculated from specific surface area data with the



Table 3

Chemical analysis of copper powders produced through glycerol process

Copper compound	Impurity content (wt.%)		
	Oxygen	Carbon	Hydrogen
Oxide	0.5	0.3	0.044
Hydroxide	0.2	0.11	0.016
Acetate	0.2	0.44	0.009

assumption that the powder comprises of spherical monosized particles. However, the SEM photomicrographs of the copper powders reveal that glycerol process yields spheroidal particles with faceted structure. Hence, the lower calculated particle size of the copper powders obtained from the  $S_{\text{BET}}$  measurements may be attributed to the spheroidal faceted structure of powder particles and spread in the size distribution.

Since the process utilizes glycerol as reducing agent and AR grade copper salts as starting compounds, the copper powder is expected to contain only oxygen, carbon, and hydrogen. The typical chemical analysis of the powders produced from different starting salts is given in Table 3. The process produces high purity copper powder having a total level of impurity content less than 1 wt.%. The glycerol process using copper acetate as starting salt yields powder with 99.7% purity. The powder produced by this process contains a thin organic surface layer, which helps to prevent the agglomeration and surface oxidation.

#### 4. Conclusions

A simple chemical process for the production of copper is described where copper precursor powder is reduced by glycerol at a temperature below the boiling point of glycerol yielding nanostructured copper powder of narrow size distribution. Out of the three compounds used, copper acetate produce copper powder of 99.7% purity having a crystallite size below 110 nm.

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