

# Characterization of Nano/Micro Size Copper Powder Bi-Product of Electropolishing process

A.M. Awad<sup>1\*</sup>, Aref M. E. Abd-El – Rahman<sup>2</sup> and M. Abdel Rafea<sup>2</sup>

<sup>1</sup>Chemical Engineering and Pilot Plant Dept., National Research Centre, Dokki, Cairo, Egypt. <sup>2</sup>Advanced Technology and New Materials Institute, Mubarak City for Scientific Research and Technology Applications, New Borg El Arab City, Alexandria, Egypt

\* e-mail: awadx1@yahoo.com

**Abstract:** **Aim:** Ultra fine copper particles were produced as a bi-product during electropolishing of copper surface. It was formed as a result of anodic oxidation of copper surface, where copper was fixed as anode and lead as cathode. It was carried out by using an electrolytic cell containing phosphoric acid 55% as the electrolytic solution. Both electrodes were connected to DC power supply to allow an electric current to pass through the solution. Anodic dissolution of copper electrode was occurred according to the applied electric potential, then Cu ions was attracted and neutralized at the surface of cathode where it was deposited in the bottom of the cell. The size of copper particles was measured by different angles SDP intensity analysis, and they were characterized by EDX and SEM analysis. [Journal of American Science 2010;6(9):137-143]. (ISSN: 1545-1003).

**Key words:** Electropolishing, Ultra fine copper, Surface leveling, Roughness, Smoothness

## 1. Introduction

Electropolishing (EP) is a highly efficient method for smoothing and brightening of metals and alloys. It has received much attention due to its practical and academic interests. Some workers tried to attain bright and smooth surface of copper by applying EP method, where humps and scratches of nano and micro size are eliminated to convert matt and rough surface to bright and smooth one [1–5].

Nano-crystalline and ultra fine copper can be produced during EP treatment, it exhibit extraordinary mechanical properties such as strength, hardness and fatigue resistance that have been the subject of widespread research [6–10].

Amongst the various conductive materials, copper has been established as an important choice because of high electrical conductivity, relatively higher melting point, excellent solderability, low electrochemical migration behavior and low materials cost [11,12]. Copper/copper oxide submicron and nano-size particles are at present of great interest in several fields of chemistry and of material science. Some features of conducting, optical and catalytic properties of small Cu/CuO particles and their possible fields of use have been reported [13–16].

Applications of copper powder include self-lubricating bearings, electrical parts, conductive epoxy, widely used as catalysts in chemical formulations and for the production of copper compounds, metal-bonded abrasive wheels and

cutting tools and aircraft braking systems. Ultra-fine copper powder was also offered for new developing

opportunities such as metal injection molding, electronics, ceramics and thick/thin film applications [17].

According to the fast developments in electronic industries, there is a great, unprecedented demand for high-strength, high conductivity materials. The technology of making conductive thick films from high purity crystalline copper powders is of considerable importance in the manufacture of electronic devices, such as hybrid integrated circuits and multilayer ceramic capacitors (MLCC) [18-21].

A chemical–mechanical method can be used for the formation of the flake copper particles, which could meet the requirement of copper thick film paste [22].

Flake copper powders could be prepared with the two-stage method. Firstly, precursor copper particles were produced by electrolytic method [23], pyrolysis [24], atomized process [25] or chemical-reduction method [26]. Secondly, the spherical copper particles are processed by a high energy ball mill. Precursor particles are extruded by ball milling media, and the flake particles could be achieved.

Vinogradov et al. [27] fabricated ultra fine grain pure copper (purity 99.98%) of 200 nm in size by the equal channel angular pressing (ECAP), and investigated the fatigue behavior of ultra fine grain pure coppers, depending on the recovery phenomenon

of non equilibrium grain boundaries after the annealing treatment at 200 C.

While, Lee et al. [28] fabricated ultra-fine-grained pure copper by the accumulative roll bonding and annealing treatment, analyzed their microstructures, and evaluated quasi-static tensile properties.

Copper powder was also prepared chemically by adding monoethanolamine to slurry comprising finely divided particles of a solid copper containing precursor compound selected from copper salt, copper carbonate, copper hydroxide, cupric oxide, or cuprous oxide, wherein the temperature is between 90 and 150 C for a time sufficient to convert the precursor compound to a copper powder [29].

The novelty of the present work is the utilization of nano/micro size copper powder produced during electropolishing of copper components whether, plates, rods, or wires in a simple electrochemical system to be used in essential applications. Also, it was studied as an economic method for separation and recovery of deposited copper without addition of external chemicals before drainage to water effluents.

## 2. Material and Methods

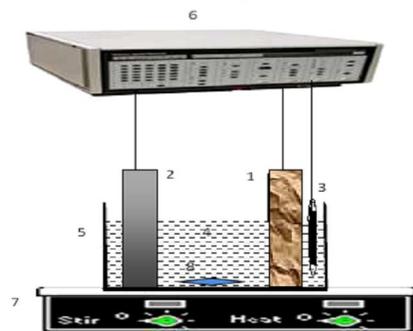
### 2-1 Materials and Apparatus

Copper sheet 99.99 % was cut into small samples with a dimension 4 x 2.5 cm and each sample was degreased before treatment by rinsing with acetone, tap water, and then distilled water.

A glass cell 15 x 7.5 x 8 cm was used for the performance of EP process, where sample was fixed as the working electrode, lead plate as a counter electrode and saturated calomel electrode (SCE) as a reference electrode, as shown in Fig.1.

The relation between electric potential and current was measured by EG&G Potentiostat/Galvanostat (Applied Princeton Research) Model 273A, driven by software M352/252 Corrosion, where a stagnant solution of prepared 55 %  $H_3PO_4$  was used as electrolytic solution.

A magnetic stirrer (PMC-BARNSTEAD/THERMOLYNE-USA) was used for agitation of electrolytic solution, where electrolytic solution was mixed well for 5 min to have a homogenous solution, then agitation was stopped before starting anodic dissolution in a stagnant solution.



**Fig. 1: A schematic diagram of experimental set up**

**1) working electrode 2) counter electrode 3) reference electrode (SCE) 4) electrolytic solution + Additives 5) glass electrolytic cell 6) Galvanostat/Potentiostat 7) magnetic stirrer 8) magnet**

### 2-2 Separation

The deposited copper powder in the bottom of the cell and remain copper powder at the surface of walls and electrodes was washed by distilled water, and decanted into a settling beaker for precipitation. The powder was separated by decantation, and washing three times by distilled water to get rid of phosphoric acid. Then copper powder was concentrated by disposing of excess water, and then it was put into a glass dish for drying in a furnace for 15 min at 110 C. The product after drying was weighted by a digital electronic balance (Precisa 205A, Suner Bal-Series) and the weigh per surface area of copper surface was determined ( $mg/cm^2$ ).

The recovery based on gravity, where the whole non dissolved UF copper was settled down in the bottom of acid solution. Most amount of acid was withdrawn by suction pump and the few remain amount of acid was diluted with distilled water three times by washing, settling, and acid suction. Finally UF copper wetted with distilled water was dried and weighed.

### 2-3 Characterization

Particle size of prepared ultra fine copper powder was measured by using N5 Submicron particle size analyzer He-Ne Laser Beam BEKMAN COULTER Miami, Florida

The surface morphology and purity of copper particles was investigated by SEM and EDX analysis by using JEOL – JSM – 636 DLA Scanning Electron Microscope, Accel Volt (kV): 20

### 3. Results and Discussion

The amount of  $\text{Cu}^{2+}$  ions are generated by the anodic dissolution of copper electrode during electropolishing process according to Faraday formula:

$$C = M I t / zF$$

where C is the theoretical concentration of  $\text{Cu}^{2+}$  (g), I electric current (A), t is the time (s), z is the chemical equivalence, F is the Faraday constant (C/mol), and M is the molecular weight of copper (g/mol) [30].

The theory of electropolishing method is based on the anodic dissolution of copper surface and if the applied conditions such as current density, temperature, and concentration are suitably chosen, copper ions are regularly dissolved, where the surface smoothness and brightness are improved.

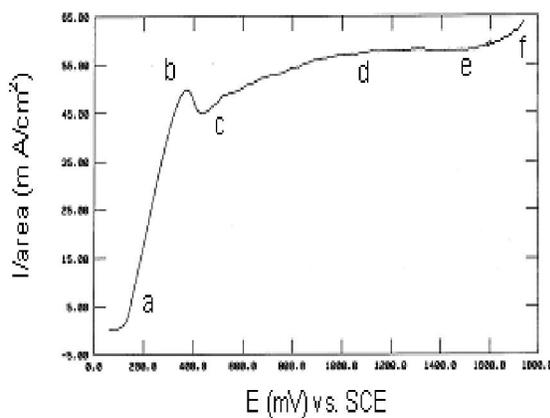
Improvement of both brightness and smoothness of copper surface by EP, and hence the amount of reddish ultra fine copper deposited are highly dependent on the applied conditions such as, current density, time, temperature and concentration of electrolytic solution

#### 3-1 Mechanism

The mechanism of EP process for different metals and alloys was investigated by some workers, where they showed that each metal or alloy has a distinct behavior during EP [31, 32].

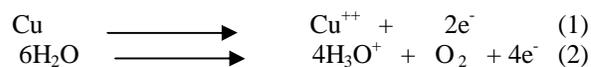
In the present study, it was observed during EP of copper under the applied electric potential that a dark layer was firstly formed over the surface. Then, after a few minutes, it was decomposed, where a homogenous and regular removal of dark layer was occurred, leaving a shiny and smooth surface.

As shown in Fig.5, the polarization curve tracked EP treatment of copper with the increase of electric potential pass through the following steps:



**Fig. 5: Polarization curve of the EP treatment of copper in a range from 0 to 1800 mV**

\*- Activation step (a-b) where the current was sharply increased due to both anodic oxidation of outer surface and ionization of water molecules (Eq. 1, 2).



\*- Neutralization step (b-c) is characterized by the decrease of current and total covering of the surface by very thin oxide/hydroxide film (Eq. 3).



\*- Stripping step (c-d): is accompanied by slightly increase of electric current, where a slowly electrochemical decomposition of oxide/hydroxide film (dark layer) was occurred regularly leaving a bright copper surface (Eq. 4).



\*- Polishing step (d-e) is characterized by the stability of electric current and a stagnant plateau due to the presence of two equal opposite reactions namely:

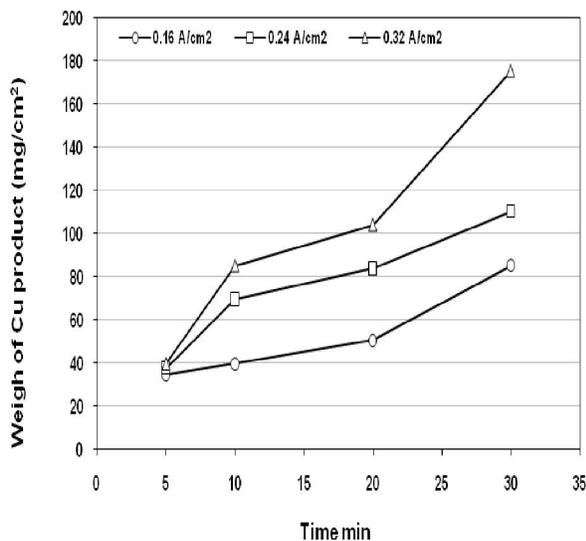
a) Filling up of the surface cavities and depressions (Eq.3), and

b) Decomposition of the surface humps and peaks accompanying by oxygen gas evolution (Eq.4).

\*- High dissolution region (e-f) is characterized by an increase of electric current density where an aggressive oxidation reaction and high loss of copper surface takes place.

#### 3-2 Influence of time and current density

Electropolishing process was studied in a wide range of time from 5 to 30 min with the condition of applying an appropriate current density. As shown in Fig.2, a slightly few amounts of UF copper (35-40  $\text{mg}/\text{cm}^2$ ) was produced by using very short time 5 min in spite of current density variation from 0.16 to 0.32  $\text{A}/\text{cm}^2$ , i.e a short time 5 min is not adequate for the dissolution of high amount of copper ions and removal of surface imperfections at different current densities.



**Fig. 2: Effect of time on the amount produce of ultra fine Cu by using different current densities 0.16, 0.24, and 0.32 A/cm<sup>2</sup>**

While, by using a longer time 10 min, the amount of UF copper produced was increased to 39.84 , 69.6 and 85.28 mg/cm<sup>2</sup> by applying higher current densities 0.16, 0.24, and 0.32 A/cm<sup>2</sup>, respectively, where more improvement of the surface was achieved.

Also, by increasing time to 20 min, more amount of UF copper was obtained 50.72, 84, and 104.16 mg/cm<sup>2</sup>, respectively while it showed the maximum amount produced 175.52 mg/cm<sup>2</sup> after 30 min by using current density 0.32 A/cm<sup>2</sup> where, a critical level of the surface treatment called High dissolution region (e-f) was attained.

This indicates that the amount of UF copper produced is increased by using higher current densities and longer time, where excess anodic dissolution of copper was occurred leading to more copper ions neutralization at the surface of cathode, which deposited finally as UF copper powder.

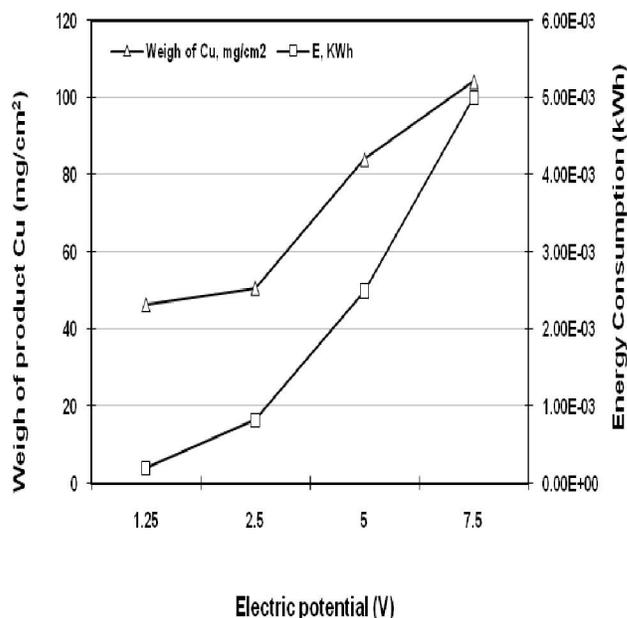
### 3-3 Influence of electric potential

The effect of applied electric potential on both amount produced ultra fine copper and the electric energy consumed was studied at constant time 20 min, concentration of H<sub>3</sub>PO<sub>4</sub> 55 %, and temperature 25°C.

The applied electric potential governs the values of limiting current and UF copper dissolved, where the region according to the polarization curve determines the improvement of both surface smoothness and production of copper in nano-micro size. The amount of UF copper produced was

46.4 mg/cm<sup>2</sup> at low potential 1.25 V with low surface smoothness, and it was gradually increased to 104.16 mg/cm<sup>2</sup> at potential 7.5 V, as shown in Fig.3. This result implies that the increase of potential leads to overcome the resistance and stimulate the ionic migration and anodic dissolution reaction. On the other hand, the electric energy consumption was increased from 0.0003 to 0.0049 KWh, where the increase of potential (V) leads to increase of electric current (I) at constant time 20 min, so the calculated E was increased according to the relation:

$$E = V * I * t$$

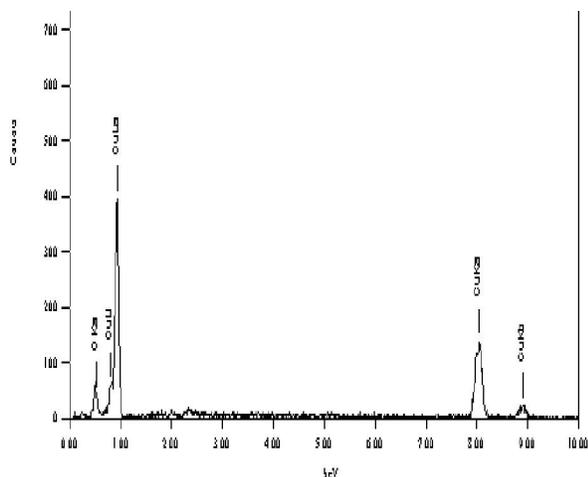


**Fig. 3: Effect of electric potential applied on both amount produced of UFC and electric energy consumption**

### 3-4 EDX Analysis

As shown in Fig. 4, EDX analysis showed three peaks appeared at 1, 8, and 9 keV, which characterized the presence of 91.12 % of the sample produced of UF copper. A small one peak at 0.5 keV revealed the presence of some traces of oxygen 8.87 %, indicating the presence of traces copper oxide. It may be produced during EP process or by environmental moisture oxidation after drying and storage, where oxidation of nano-micro size particles with a high surface area is difficult to control.

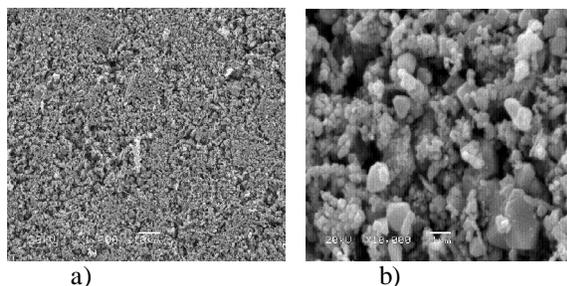
According to these results, the produced UF copper showed a high purity of copper 91.12 % and trace 8.88 % CuO which indicates the efficiency of electrochemical method for producing a highly grade of resalable copper for different applications.



**Fig. 4: EDX Analysis of the produced UF copper**

3-5 SEM Analysis

From SEM photograph as shown in Fig. 5, The uniformity of particles is shown in Fig. 5-a, where its low particle size, and spherical shape allow the homogenous distribution, while in case of Fig. 5-b, with higher magnification, it can be distinctly observed that the ultra-fine, mono-dispersed, non-agglomerated copper particles were produced, and a spherical particles, high porosity, and very fine particles are appeared.

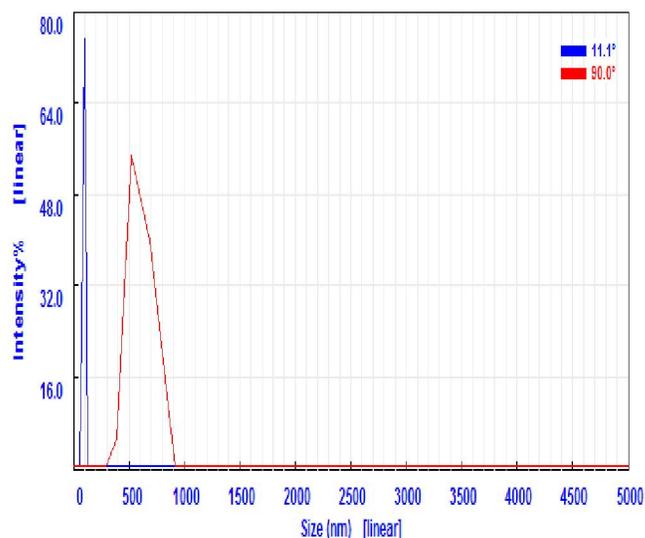


**Fig. 5: SEM Analysis of the produced UF copper: a) magnification x 1000 b) magnification x 10000**

3-6 Measurement of particle size by SDP

The particle size of a UF copper sample produced by electropolishing process was measured to evaluate its characteristics and its applications suitable for. Different Angle SDP Intensity analysis was used for measuring the particle size of UF copper particles. As shown in Fig. 6, it revealed that the particle size is ranged between 300 and 900 nm, while almost particle size revealed the mean particle size at 577.6 nm as shown in SDP results summary, table-1. The variation of particle size is demonstrated as a result of the different steps during electropolishing process where, electrode potential was increased with continuous treatment and accordingly, the current

density is varied as shown in polarization curve. Each level of potential and current is characterized by distinct reactions over copper surface. Moreover, anodic oxidation reaction is the predominant reaction and the dissolved ions are affected by velocity of ions, and diffusion coefficient.



**Fig. 6: Measurement of particle size by SDP of the produced UF copper**

The anodic dissolution of micro grams of copper is a phenomenon superimposed on electropolishing of copper surface by elimination of micro scratches and irregular humps, where the mat and rough surface converted to bright and smooth one.

**Table-1: SDP Results Summary**

Angle	Parameter	Calculated Results					
	SDP Range (nm)	Size (nm)	%amt (nm)	Std.Dev (nm)	Mean Size (nm)	Mean SD (nm)	%Dust
11.1°	1.0-5000.0	88.4	100.00	11.9	88.4	11.9	0.000
90.0°	1.0-5000.0	577.6	100.00	110.4	577.6	110.4	38.807

The deposited copper into the electrolytic solution as sludge after EP processes represent a big environmental problem if it is discharged into lakes, rivers, or water surface. So, it is necessary to separate UF copper by settling, washing, concentrating, and drying. Filtration step was avoided due to the highly adhesion of UF copper, where a part of UF copper can be lost by adhesion with filter material. The success recovery of UF copper for application in strategic fields makes the EP process acquire more economic view and require reappraisal in industrial sectors.

#### 4. Conclusion

Electropolishing of copper surface was accompanied by anodic dissolution of copper ions, which neutralized and settle down into the electrolytic cell. The amount produced of UF copper is highly dependent on current density, and time, where 175.5 mg/cm<sup>2</sup> was produced by using 0.32 A/cm<sup>2</sup> and 30 min, while 34.7 was produced by using 0.16 A/cm<sup>2</sup> and 5 min. Analysis of EDX and SEM showed the purity of UF copper and the presence of non agglomerated spherical particles. The separation and characterization of UF copper produced revealed the presence of nano/micro particle size. Measurements by using SDP method revealed the presence of 300 – 900 nm with mean value 578 nm of particle size, which indicate the possibility to exploit in some essential applications.

#### Corresponding author

.M. Awad

Chemical Engineering and Pilot Plant Dept., National Research Centre, Dokki, Cairo, Egypt  
e-mail: awadx1@yahoo.com

#### 5. REFERENCES

- Bing Dua, Ian Ivar Suni, J. Electrochem. Soc. 151, 6 (2004)
- V. Vignal, J.C. Roux, S. Flandrois, A. Fevrier, Corros. Sci. 42, 1041(2000)
- D. Sazou, Electrochim. Acta 42, (4) 621(1997)
- G.L. Wynick, C.J. Boehlert, Mater. Characterization, 55, 190 (2005)
- A.M. Awad, N.A. Abdel Ghany, T.M. Dahy, Applied Surface Science 256, 4370–4375(2010)
- Gleiter H. Prog Mater Sci;33:223–315 (1989).
- Weertman J. In: Koch, editor. Nanostructured materials. Norwich, NY: Noyes; p. 393–417(2002)
- Meyers MA, Mishra A, Benson DJ. Prog Mater Sci; 51:427–556 (2006)
- Meyers MA, Mishra A, Benson DJ. JOM (April):41–8 (2006)
- Koch CCI, Ovid'ko A, Seal S, Veprek S. Structural nanocrystalline materials. Cambridge: Cambridge University Press; (2007).
- Wu, S.P., Jiao, L., Ni, J., Zeng, Z.O., Liu, S., "Preparation of ultra fine copper–nickel bimetallic powders for conductive thick film". Intermetallics 15 (10), 1316–132 (2007)
- Wu, S.P., "Preparation of ultra-fine copper powder and its lead-free conductive thick film" Mater. Lett. 61 (16), 3526–3530 (2007)
- D. Das, T.K. Kundu, M.K. Dey, S. Chakraborty, D. Chakravorty, Proc. Indian Acad. Sci. (Chem. Sci.) 115, 341(2003)
- N.A. Dhas, C.P. Raj, A. Gedanken, Chem. Mater. 10, 1446 (1998)
- E.R. Leite, N.L.V. Carreno, E. Longo, A. Valentini, L.F.D. Probst, J. Nanosci. Nanotechnol. 2 , 89 (2002)
- Labande, J. Ruiz, D. Astruc, J. Am. Chem. Soc. 124, 1782 (2002)
- Klaine, S.J., Alvarez, P.J., Batley, G.E., Fernandes, T.F., Handy, R.D., Lyon, D.Y., Mahendra, S., McLaughlin, M.J., Lead, J.R., Nanomaterials in the environment: behavior, fate, bioavailability and effects. Environmental Toxicology and Chemistry 27, 1825–1851(2008)
- Chien-Yu Huang, Shyang Roeng Sheen, Materials Letters 30, 357–361(1997)
- Sinha Arvind, Swapan Kumar Das, T.V. Kumar, Journal of Materials Synthesis and Processing 7 (6) 373–377(1999)
- Sinha Amit, B.P. Sharma, Materials Research Bulletin 37, 407–416 (2002)
- G.M. Chow, L.K. Kurihara, K.M. Kemner, E. Schoen, W.T. Elam, A. Ervin, S. Keller, Y.D. Zhang, J. Budnick, T. Ambrose, Journal of Materials Research 10 (6) 1546–1554 (1995)
- S.P. Wua, R.Y. Gaob, L.H. Xua, "Preparation of micron-sized flake copper powder for base-metal-electrode multi-layer ceramic capacitor", journal of materials processing technology 20 9, 1129– 1133 (2009)
- Xue, J.Q., Wu, Q., Wang, Z.Q., Yi, S.F., "Function of additives in electrolytic preparation of copper powder", Hydrometallurgy 82 (3–4), 154–156 (2006)
- Rosenband, V., Gany, A., "Preparation of nickel and copper submicrometer particles by pyrolysis of their formats" J. Mater. Process. Technol. 153–154, 1058–1061(2004)
- Karibyan, A.N., Medvedovskii, A.B., Belyakov, V.A., et al., Atomized copper powders. Sov. Powder Metall. Met. Ceram. 20 (5), 316–319 (1981)
- Sinha, A., Sharma, B.P., "Preparation of copper powder by glycerol process. Mater. Res. Bull. 37 (3), 407–416 (2002)
- Vinogradov, Y. Kaneko, K. Kitagawa, S. Hashimoto, V. Stolyarov, R. Valiev, Scripta Mater. 36, 1345 (1997)

28. C.G. Lee, K.J. Kim, S. Lee, K. Cho, Metall. Trans. 29A, 469 (1998)
29. Gang Zhao , Michael P. Pompeo , US 7517382 B2 , Apr. (2009)
30. M. Buhlert, Ph.D., Elektropolieren und Elektrostrukturieren von Edlstahl, Messing und Aluminium, Bremen Uni., (2000)
31. M. Buhlert, M. Gartner, M. Modreanu, A. Jitianu, R. Gavrilă, A. Awad, P.J. Plath, Galvanotechnik, 95 (7), 1629 (2004)
32. A.M. Awad, Ph.D., Optical characterization of spectrally selective anodically coated electrolytically colored and polished aluminum surfaces, Ain Shams Uni., (2004)

5/6/2010