

## The effect of process parameters on copper powder particle size and shape produced by electrolysis method

Mustafa Boz<sup>\*1</sup> and Masood Hasheminasari<sup>2a</sup>

<sup>1</sup> Technical Education Faculty (Metal Education), Karabük University, Karabük, Turkey

<sup>2</sup> Faculty of Engineering (Metallurgical and Materials), Colorado School of Mines, Colorado, USA

(Received November 22, 2012, Revised May 26, 2013, Accepted June 07, 2013)

**Abstract.** In this study, an electrolyzing device for the production of metal powders was designed and fabricated. The production of copper powders was performed using a variety of current densities, anode-cathode distances and power removal times. The effect of these parameters on powder particle size and shape was determined. Particle size was measured using a laser diffraction unit while the powder shape was determined by SEM. Experimental results show that an increase in current density leads to a decrease in powder particle size. In addition particle shape changed from globular dendritic to acicular dendritic with increasing the current density. Distance between the cathode and anode also showed a similar influence on powder particle size and shape. An increase in time of powder removal led to an increase in powder particle size, as the shape changed from acicular dendritic to globular dendritic.

**Keywords:** metallurgy, electrolytic copper powder, current density, powder particle size and shape

---

### 1. Introduction

In powder production, optimum selection of process parameter is essential in order to obtain desired morphology and shape. Features of the powder such as size and shape can be estimated based on the process parameters. Almost all materials can be powderised, but the proper method is material dependent and is influenced by cost, particle reactions and desired features. There are four commonly used methods in production of metal powders such as mechanical grinding and alloying, chemical method, atomization and electrolysis (Pavlović *et al.* 2001, Boz and Kurt 2009).

Powders may accumulate on a cathode of an electrolysis cell under certain working conditions. Copper, chromium, iron, zinc, manganese, palladium and silver can be produced by electrolysis. Electrolytic method accounts for one or two percent of the global market in powder production. The main advantage of this method is its high product purity (German 2007, Marković *et al.* 2002). In powder production, an electrolyte bath consisting of copper sulphate, sulphuric acid and pure water is used with additions of boric acid to prevent the covering of the cathode with copper powders (Lee *et al.* 1998).

With an applied external electrical current dissolution in electrolyte is called Electrolysis.

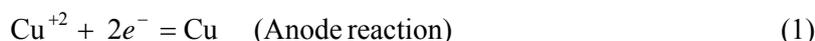
---

\*Corresponding author, Assistant Professor, E-mail: [mboz@gmail.com](mailto:mboz@gmail.com)

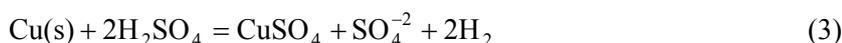
<sup>a</sup> Ph.D. Student, Ph.D., E-mail: [mhashemi@mines.edu.tr](mailto:mhashemi@mines.edu.tr)

According to Arrhenius classical theory an electrolyte consists of ions that are free (liberated) electrical particulates. In the dissolution of the electrolyte, formed ions are negative or positive along with charged atoms and atom groups. The movement of the ions in an electrical field provides transmission of current (German 2007).

In production of copper powders, two electrodes are connected to poles of a generator immersed in an electrolyze cup. As electrons are released from the negative pole of the cathode generator, a portion of electrons in the anode is also extracted to the positive pole of the generator. The positive ions arriving at the cathode, take sufficient electrons for their neutralization. Negative ions that are transmitted to the anode transform to a neutral state by donating their electrons to the anode. In time, as shown in Eqs. (1) and (2), the number of electrons that are given to anode is equal to the number of received electrons from cathode (Klar 1984).



Neutralized ions and electrons transform to a state of atom and atom groups, and change their chemical properties. They are either liberated or can change the electrodes, electrolyte or electrolyte solvent. These are called secondary reactions that are formed in every electrolyze event, according to the type of electrodes and electrolytes.



The electrolyte bath in the Electrolyze method is made of pure water, sulphuric acid, copper sulphate. As shown in Eq. (3), copper sulphate provides copper ions; sulphuric acid provides hydrogen ions that increase the electrical conductance of the solution. The addition of boric acid to the bath decreases the buildup of copper on the cathode (Klar 1984).

An increase in current density is dependent on increasing of the copper powder on the cathode and decreasing concentration of copper in the cathode center. With increases of copper concentration in the electrolyte process, bigger powder particulates are produced. Increases of sulphuric acid density led to increase of dendritic powder quantity. Changing in the electrolyte temperature will affect the movements of ions hence enhancing diffusion rate in the solution. The existence of foreign ions in electrolyte is undesirable as, they will decrease powder on cathode and collected powder of copper volume (Pavlović *et al.* 2001, Incekara *et al.* 2008).

In the electrolysis process, with the application of a voltage, the metal ions dissolved on the anode pass through electrolyte and accumulate on the cathode. Porous powder deposits on the cathode are peeled, washed, dried, ground and powderised. Heat treatment is applied in order to reduce surface tensions and remove volatile materials. Powders produced with the electrolysis method generally feature a dendritic or sponge-like shape. Particle size and shape can be controlled to a considerable extent and have some dependence on the bathing conditions and process procedures (Đuršinová 1991, Lenina 1994).

Quality of the produced electrolytic copper powder is determined by several factors, including the combination of electrolyte, temperature of electrolyte, current density, type and size of anode and cathode, distance between anode and cathode, existence of foreign ions in electrolyte and removal time of the powder on cathode (Pavlović *et al.* 2001, Đuršinová 1991, Popov *et al.* 2002, Agrawal *et al.* 2007). Demand for electrolytic copper is rapidly increasing; however growth in the

industry is somewhat limited due to a lack of extensive research in the process. Therefore this study aims to evaluate using scrap-copper for electrolysis production, as well as examining the effect of current density, anode-cathode distance and powder removal time on the shape and size of the copper powder product.

## 2. Experimental procedure

In this study, Cu powder production was conducted with an electrolysis device. The practicality of producing commercially pure powder from scrap copper was examined. Powder production was carried out using the following parameters: Current Density (between 531-3571 A/m), Anode-Cathode Distance (4, 8, 12 and 16 cm) and times of powder removal (5, 10, 20, 30 and 40 min).

The electrolysis device used in the experiments was designed and manufactured by the author using the facilities at Karabük University. This device is schematically shown in Fig. 1 and has an electrolyte capacity of 30 liters. The electrolyte container is made of glass and becomes narrower at the base. This device consists of an anode and a cathode, an electrolytic liquid, a heater, a powder collection container, a pump that mixes electrolytic liquid and an adjustable power source to ensure flow.

As shown in Table 1, the electrolyte liquid consisted of copper sulphate, sulphuric acid and pure water. Copper sulphate was added into pure water and mixed until fully dissolved. Boric acid and then sulphuric acid were added to this solution at predetermined ratios.

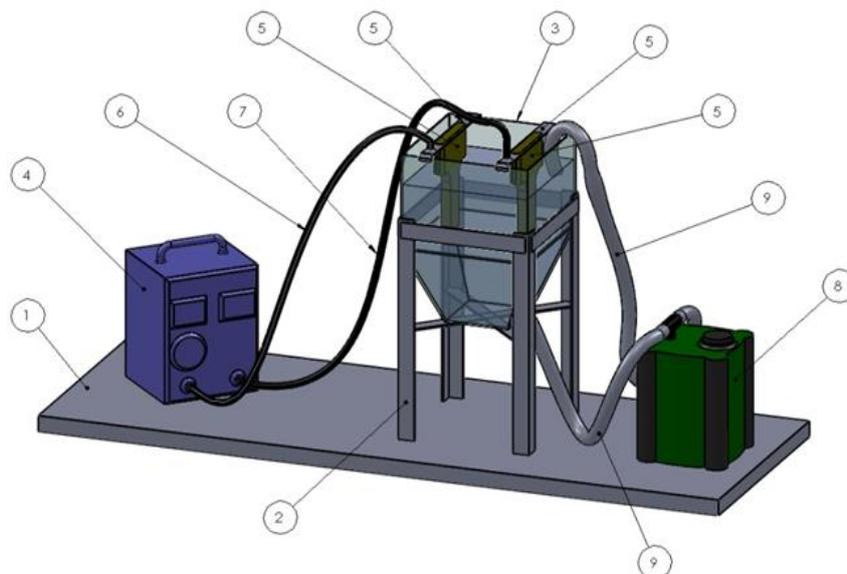


Fig. 1 Schematic illustration of the electrolysis device. (1) Lower platform, (2) electrolysis container legs, (3) electrolyses container, (4) power source, (5) copper electrodes (anode and cathode), (6) (+) pole, (7) (-) pole, (8) filter and circulation pump, (9) filter hoses

Table 1 Mixture ratio of electrolytic liquid

Component	Formula	Concentration (g/lt)
Copper sulphate	CuSO <sub>4</sub>	38
Sulphuric acid	H <sub>2</sub> (SO <sub>4</sub> )	150
Boric acid	H <sub>3</sub> BO <sub>3</sub>	4

Scrap copper was used in the anode and cathode due to its low cost and recycling attributes. Surface area of the anode ranged between 0.0085 and 0.0095 m. In the literature, it is shown that electrolytic tanks of different types and features like ceramic, reinforced plastic, plastic-lined steel and glass can be successfully used (Pavlović *et al.* 2001). In this study, a glass tank was chosen based on the availability and cost.

A large anode area can cause transfer of excessive Cu ions to the solution, which can increase the CuSO<sub>4</sub> ratio in the solution. It poses the risk of reducing acidity and conductivity of the solution and excessive copper sulphate sedimentation. For this reason, a 1:1 ratio of anode area to cathode area was used in this study.

An acidic copper sulphate bath can be used at temperatures between 22 and 49°C, and can be operated at higher temperatures when needed. The temperature of the electrolytic liquid was held at 42 ± 3°C as to maintain the conductivity of the solution at appropriate values.

The produced copper powder was washed in an ammonium hydroxide (NH<sub>4</sub>OH) baths with pH values of 7, 5 and 9 after removal from the electrolyte. It was then transferred to an aqueous solution consisting of Benzotriazole (C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>) at 0, 4% ratio to prevent oxidation of powders. The copper powders taken from the Benzotriazole were dried for eight hours at room temperature under normal atmospheric conditions.

After the produced copper powders were dried, they were decomposed so that they could be examined using scanning electron microscopy (SEM). A Turbula T2C mixing device, which can move in three dimensions, was employed for mixing the produced powders. A Jeol 6060 LV SEM was used to study the morphology and shape of the particles. Particle size analysis was performed so that the powder dimension could be determined. Particle size distribution of the powders was determined by using Malvern Mastersizer E type laser particle diffraction device.

### 3. Experimental results and discussions

#### 3.1 Current density

The amounts of copper powders produced in weight are given in Table 2. These powders were obtained using various current densities and a 45-minute powder removal time. The distance between the anode and cathode was 12 cm.

It is shown in Table 2 that increasing current density on the cathode increased the produced powder amount considerably. Table 2 also shows that the amount of copper produced for 45 min is 6 g at 531 A/m<sup>2</sup>, while the amount of copper is 44 g at 3571 A/m<sup>2</sup>. According to Faraday's Law,

Table 2 The amounts of copper powder particles produced in weight for 45 min at 12 cm anode and cathode distance

Current density (A/m <sup>2</sup> )	The amounts of copper powder particles produced for 45
531	6 g
1064	12 g
1685	22 g
2247	34 g
2976	40 g
3571	44 g

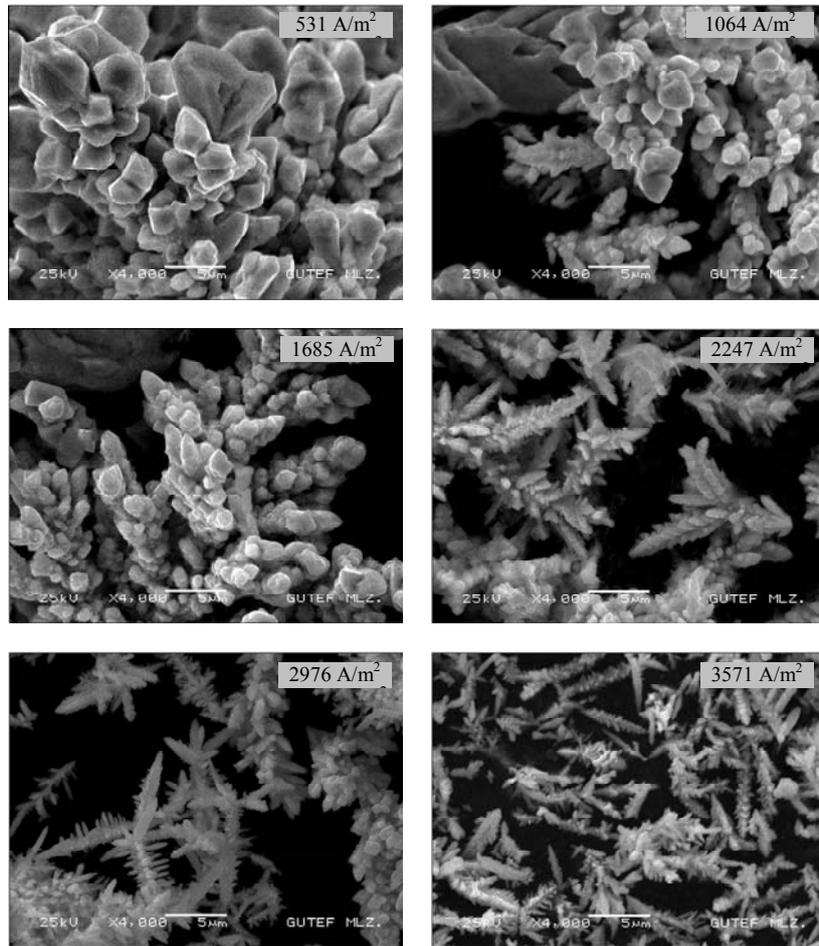


Fig. 2 The effect of current density on powder particle shape

an increase in current density will increase the solute substance amount. It is considered that the reaction speed depending on increasing current density had influence and this, in turn, increased the amount of powder produced. The produced copper powders were blended in the Turbula T2C

mixer to obtain a homogeneous mixture. The SEM images of the copper powders obtained as a result of the blending are illustrated in Fig. 2.

The SEM images in Fig. 2 show that the copper particles generally have dendritic structure. Āurišinová (1991) investigated the influential parameters on the quality of electrolytic copper particles and showed that the particles formed are basically acicular, globular and tubular in shape. It is shown that the dendritic particle structures vary between acicular, globular and tubular forms. These results are in agreement with those found in literature. It is seen from Fig. 2 that the particles are plate-like at current densities of 531 and 1064 A/m<sup>2</sup> while they are almost globular at 1685 A/m<sup>2</sup>. Globular particles are seen at the current densities of 2247 A/m<sup>2</sup> with some smaller

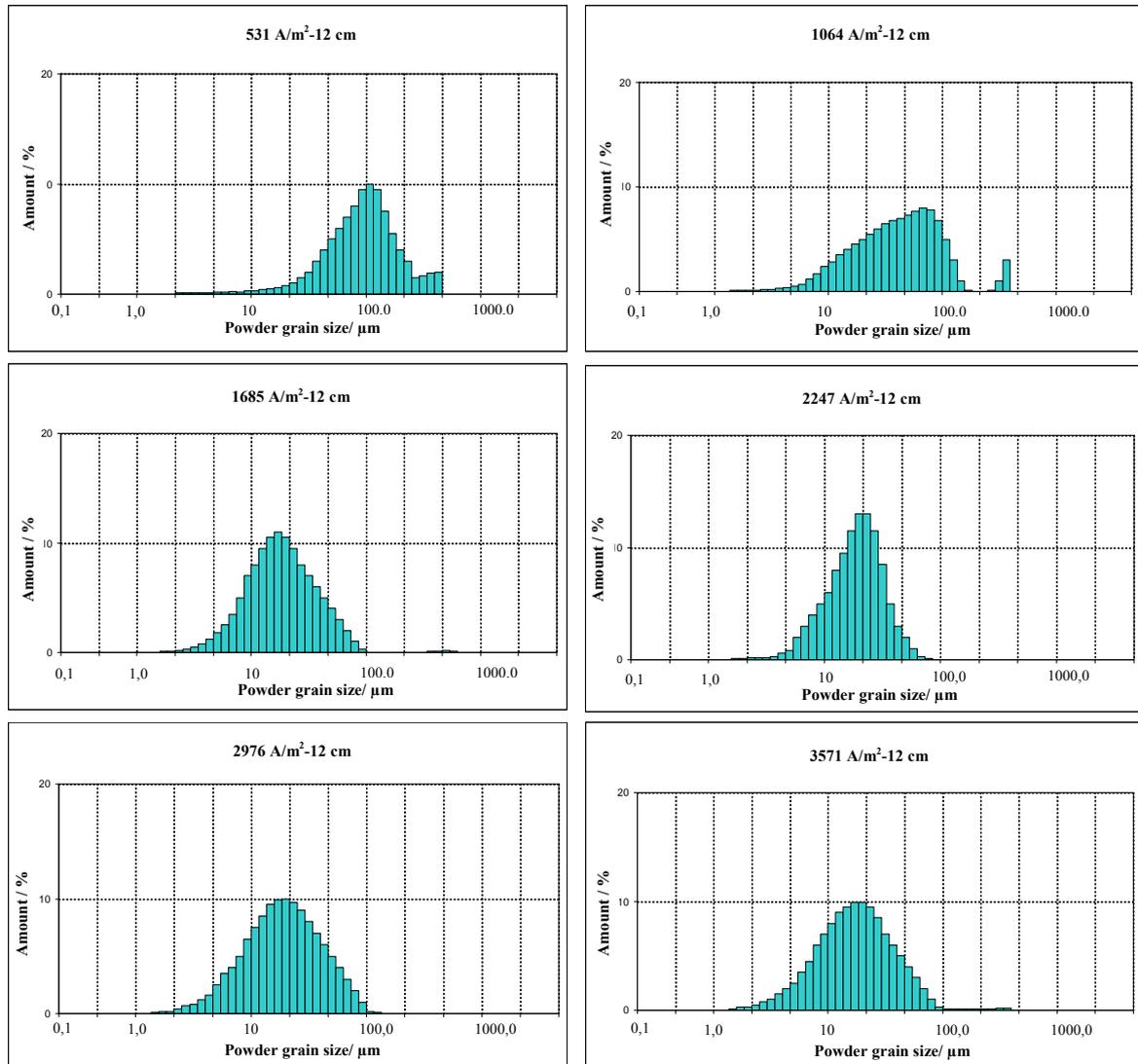


Fig. 3 The effect of current density on powder particle size

globular particles. However, formations of acicular dendrites at relatively high current densities ( $3571 \text{ A/m}^2$ ) can also be shown in Fig. 2. It was determined that increasing current density decreased the dendritic arm growth. This can be attributed to the short reaction time at high current densities. When the time is short, the particles cannot move to the other sides and orient themselves randomly. Fig. 3 shows the average powder particle size distribution depending on current density.

İncekara *et al.* (2008), Boz and Kurt (2011) and Popov *et al.* (2003) carried out a study on production of electrolytic copper powder particles and stated that average powder particle sizes varied between  $9$  and  $150 \mu\text{m}$  at  $1800$  and  $3600 \text{ A/m}^2$ . However, Ďurišínová (1991) and Orhan and Hapçı (2010) stated that larger copper powder particles can be produced at lower current densities.

In this study, although the average powder particle sizes varied between  $1$  and  $600 \mu\text{m}$ , powder particles below  $1 \mu\text{m}$  were also observed. However, these small powder particles could not be collected from the electrolytic liquid. Provided the distance between anode cathode remained constant at all the tests, the average powder particle size was found to be  $128.25 \mu\text{m}$  at  $531 \text{ A/m}^2$ . Depending on the increasing current density, the average powder particle sizes of  $96.66 \mu\text{m}$ ,  $61.8 \mu\text{m}$ ,  $52.94 \mu\text{m}$ ,  $37.57 \mu\text{m}$  and  $37.9 \mu\text{m}$  were obtained at  $1064 \text{ A/m}^2$ ,  $1685 \text{ A/m}^2$ ,  $2247 \text{ A/m}^2$ ,  $2976 \text{ A/m}^2$  and  $3571 \text{ A/m}^2$ , respectively. Larger powder particles were produced at lower current densities while smaller powder particles were produced at higher current densities. The reason for occurrence of small particles in higher current densities is that can be explained with an increase in the amount of nucleation on cathode and not enough time for growing of powder particles.

### 3.2 Anode-cathode distance

For the powder particle production, a constant current density of  $2976 \text{ A/m}^2$  and various distances between the poles were selected. The distances between anode and cathode were determined to be  $4$ ,  $8$ ,  $12$  and  $16 \text{ cm}$ . For each test, the powder removal time was  $45 \text{ min}$ . The produced powder particles in weight at a constant current density ( $2976 \text{ A/m}^2$ ) and various anode-cathode distances are given in Table 3.

The amounts of produced copper powder particles decrease with increasing the distance between anode and cathode provided current density remains constant. This can be explained by the decreasing of reaction speed as the result of increasing the distance between anode and cathode. The SEM images of the produced copper powder particle samples are found in Fig. 4. The SEM images were taken after they had been mixed homogeneously in Turbula T2C mixer.

In Fig. 4, a dendritic structure is observed for all the electrolytic copper powder particles produced. It is seen that acicular dendritic powder particle shape transforms to tubular dendritic

Table 3 The amounts of copper powder particles produced in weight for 45 min

The distance between anode-cathode (cm)	Powder particles produced (g)
4	46
8	44
12	44
16	42

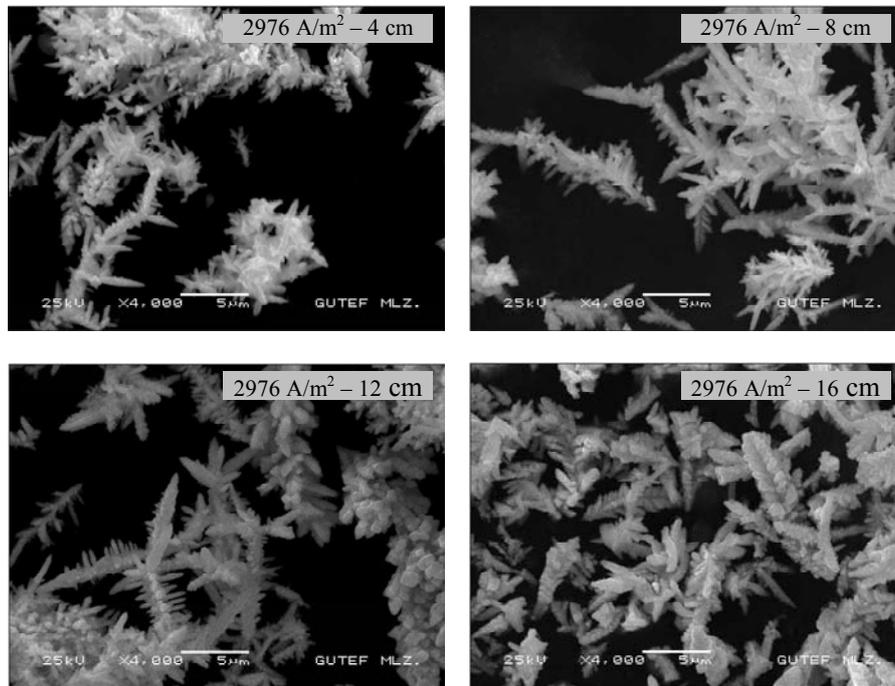


Fig. 4 The influence of the distance between anode and cathode on powder particle shape

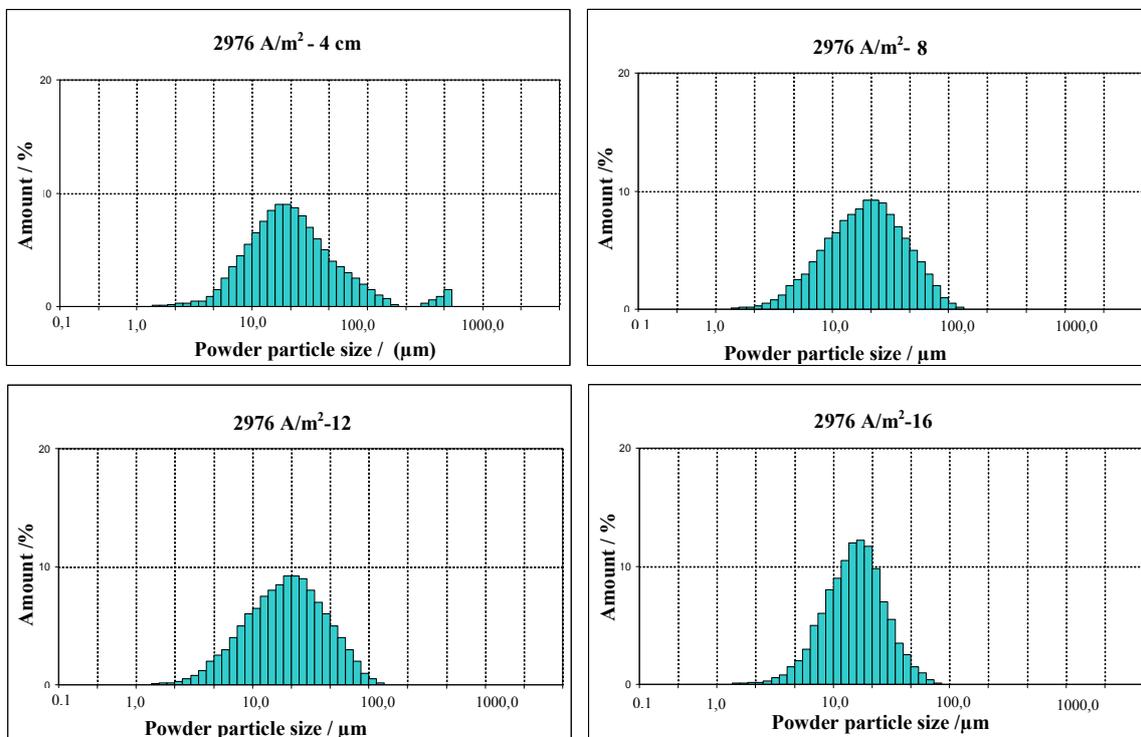


Fig. 5 The influence of anode-cathode distance on the average powder particle size

particle shape with increasing the anode-cathode distance at constant current density ( $2976 \text{ A/m}^2$ ).

Thin acicular dendrites are seen for 4 and 8 mm anode-cathode distances, while acicular dendritic structure containing globular dendrites are seen for the 12 mm anode-cathode distance. A structure mainly consisting of tubular like dendrites is dominant for 16 mm anode-cathode distance.

More densely spaced dendritic branches are seen with increasing the distance between anode and cathode. At short anode-cathode distances the copper ions detached from the anode gathered on the cathode, and they can't find enough time to fill the spaces between the dendritic branches on the first grain formed. On the other hand, long anode-cathode distance enables the powder particles to travel freely on the first grain formed on the cathode, as there is enough time for diffusion, leading to a preferred orientation.

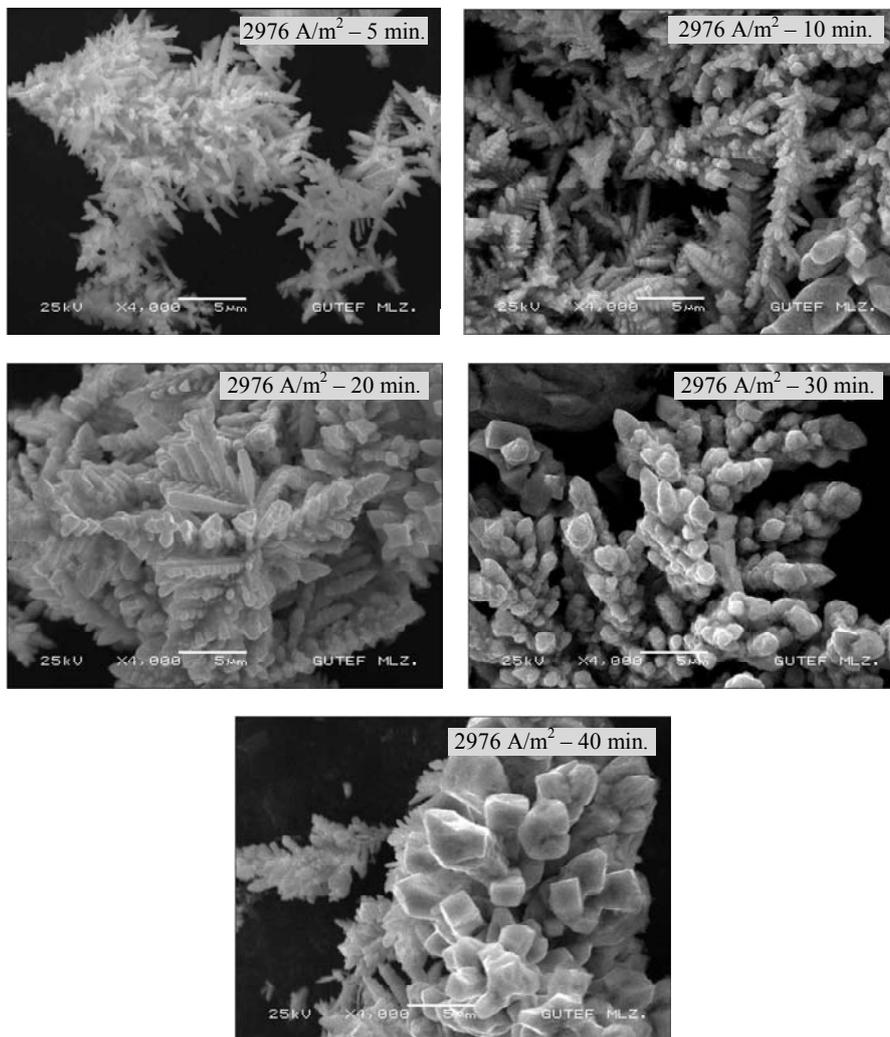


Fig. 6 The effect of powder particle removal time on powder particle shape

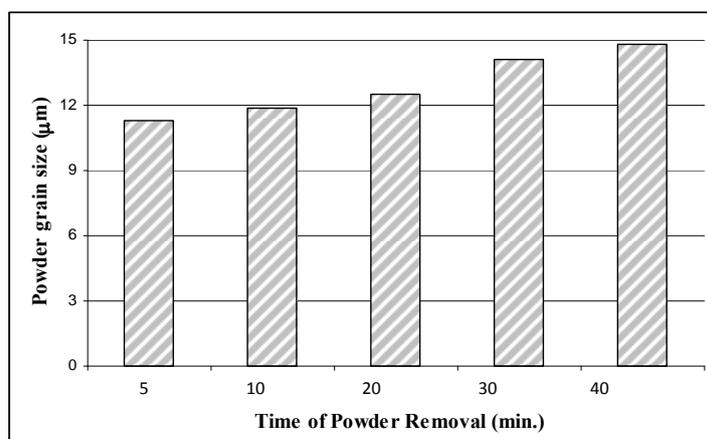


Fig. 7 Effect of number of CFRP layer on stiffness and ultimate load

Based on the distance between anode and cathode, the average powder particle size distribution is given in Fig. 5. Powder particle size varies between 1.5 and 600  $\mu\text{m}$ . Some floating powder particles were also seen on the electrolytic liquid. These powder particles were considered to be less than 1  $\mu\text{m}$  in size and could not be gathered from the cathode surface. The powder particle size is shown to increase with increasing the anode-cathode distance. At a 4 cm anode-cathode distance, average powder particle size was determined to be 25.78  $\mu\text{m}$  and at 8, 12 and 16 cm distances, average powder particle sizes were determined to be 34.15  $\mu\text{m}$ , 37.57  $\mu\text{m}$  and 50.33  $\mu\text{m}$ , respectively.

In addition, increasing powder particle size with increasing anode-cathode distance can be attributed to a slowdown in reaction speed in the electrolytic liquid. With decreasing in reaction rate, it has been shown that copper ions were deposited and growth on formed less nucleate. As a result of this, it has been considered that less but bigger particles have been formed.

### 3.3 Times of powder particle removal

For powder particle production, various powder particle removal times were chosen at a constant flow density of 2976  $\text{A}/\text{m}^2$ . The powder particle removal times used were 5, 10, 20, 30 and 40 minutes. The produced copper powder particles were blended in Turbula T2C mixer to obtain a homogeneous mixture. SEM images of the sample powder particles obtained as a result of the blending are found in Fig. 6.

It is shown that all electrolytic copper powders are in a dendritic shape. In addition, the powder particles are mainly formed acicular, globular and tabular shapes similar to the findings in the literature (Peissker 1984, Popov *et al.* 2003). At a constant current density (2976  $\text{A}/\text{m}^2$ ), increasing powder removal time changed the powder shape from acicular dendrite to tabular dendrite. At 5 and 10 minute powder removal times, acicular dendrites were observed, whereas at 20 and 30 minutes, globular and tabular dendrites were found to be dominant. At powder removal times of 40 minutes, a structure dominated by tabular dendrites was observed. In the case of increasing in powder removal time, dendrite arms were filled by new copper ions resulting in powder particles consisting of tabular dendrite instead of acicular dendrite.

Average particle size distribution dependence on the powder removal time is given in Fig. 7 at fixed current density (2976 A/m<sup>2</sup>). Average powder sizes are seen to vary between 11.31  $\mu\text{m}$  and 14.83  $\mu\text{m}$ . It was also observed that there were powders that were believed to be smaller than 1  $\mu\text{m}$  floating on the upper part of the electrolytic liquid, which could not be removed from the cathode surface. As powder removal time increases the powder size also increases. Average powder size was 11.31  $\mu\text{m}$  at 5-minute powder removal time; it was 11.55  $\mu\text{m}$  at 10 minutes, 12.33  $\mu\text{m}$  at 20 minutes, 14.41  $\mu\text{m}$  at 30 minutes and 14.83  $\mu\text{m}$  at 40 minutes. Powder size increase as a function of power removal time is likely due to presence of copper ions on the localized nucleates.

#### 4. Conclusions

The following conclusions can be drawn from the present study, which examines the influences of various production parameters of electrolysis method on copper powder particle shape and size

- Copper powder particle production can be performed through electrolysis method in laboratory conditions and powders of various shapes and sizes were obtained depending on various parameters.
- Increasing current density decreased the powder size, and the powder shape was found to change from globular dendrite towards acicular dendrite.
- At 2247 and 2976 A/m<sup>2</sup> current densities and at 12 cm anode-cathode distance, thin acicular dendritic powders were produced. These powders also contained some globular powders and can be regarded as ideal.
- At current densities above 3571 A/m<sup>2</sup>, production of copper powders is not possible from scrap copper after the initial times of 1-2 min.
- Increasing anode-cathode distance was found to increase the powder size and powder shape was also found to change from acicular dendrite to globular dendrite.
- An increase in powder removal time led to an increase in powder size, and it was observed that powder shape changed from acicular dendrite to tabular dendrite.
- As a result of our experimental data, at current densities of 3571 A/m<sup>2</sup> or above, powder production can be investigated by vibrating the anode pole suitably

#### References

- Agrawal, A., Kumari, S. Bagchi, D., Kumar, V. and Pandey, B.D. (2007), "Recovery of copper Powder from copper bleed electrolyte of an Indian copper smelter by electrolysis", *Miner. Eng.*, **20**(1), 95-97.
- Boz, M. and Kurt, A. (2009) "The effect of time of powder removal on powder particle size and shape copper powder produced by electrolysis method", *4th International Conference on Powder Metallurgy RoPM*, Craiova, Romania, July.
- Boz, M. and Kurt, A. (2011), "The effect of time of powder removal on powder particle size and shape copper powder produced by electrolysis method", *Mater. Sci. Forum*, **672**, 271-275.
- Đurišínová, A. (1991), "Factors Influencing quality of electrolytic copper powder", *Powder Metallurgy*, **34**(2), 139-141.
- German, R.M. (2007), *Powder Metallurgy & Particulate Materials Processing*, (Translation Editors: Sarıtaş, S., Turker, M. and Durlu, N.), Turkish Powder Metallurgy Association, pp.61- 97.
- İncekara, M., Boz, M., Kurt, A. and Gobuluk, M. (2008), "The effect of current density on powder particle

- size and shape copper powder produced by electrolysis method”, *5th International Powder Metallurgy Conference*, October 08-12.
- Klar, E. (1984), *Powder metallurgy, Metals Handbook*, (9th Edition), The American Society for Metals, Vol. 7, USA.
- Lee, P.W., Eisen, W.B., Ferguson, B.L. German, R.M., Iacocca, R., Madan, D. Anderow, and Hardbound, H. (1998), *ASM Metals Handbook Powder Metallurgy*, (9th Edition), Vol. 7, ASM International, Ohio, USA.
- Lenina, V.I. (1994), “Method and apparatus for copper powder production by electrolysis of sulfate solutions”, Russian Agency for Patents and Trademarks, Patent Number: RU 2022717 C1, pp. 1-6.
- Markovic, R., Songacilovic, V. and Radisavljevic, L. (2002), “Influence of Cell Geometry on Powder Characteristics”, 3, *International Powder Metallurgy Conference*, Copper Institute Boor, pp. 11-15.
- Orhan, G. and Hapçı, G. (2010), “Effect of electrolysis parameters on the morphologies of copper powder obtained in a rotating cylinder electrode cell”, *Powder Technol.*, DOI:10.1016/j.powtec.2010.03.003.
- Pavlović, M.G., Pavlović, Lj.J., Ivanović, E.R., Radmilović, V. and Popov, K.I. (2001) “The Effect of Particle Structure on Apparent density of Electrolytic Copper Powder”, *J. Serb. Chem. Soc.*, **66**(11-12), 923-933.
- Peissker, E. (1984), “Production and properties of electrolytic copper powder”, *The Int’l J. Powder Metall.*, **20**(4).
- Popov, K.I., Krstić, S.B. and Pavlović, M.G. (2003), “The critical apparent density for the free flow of copper powder”, *J. Serbian Chem. Soc.*, **68**(6), 511-513.
- Popov, K.I., Popović, Lj.J., Ivanović, E.R., Radmilović, V.M. and Pavlović, G (2002), “The Effect of Reversing current deposition on the apparent density of electrolytic copper powder”, *J. Serb. Chem. Soc.*, **67**(1), 61-67.
- Walker, R. and Duncan, S.J. (1984), “The morphology and properties of electrodeposited copper powder, *Surface Technology*, **23**(4), 301-321.