www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Arch. Metall. Mater. **68** (2023), 1, 375-386

DOI: https://doi.org/10.24425/amm.2023.141514

K. WOJTASZEK[1], F. CEBULA[1], B. PARTYKA[1], P. DESZCZ[1], G. WŁOCH[1], R.P. SOCHA[2], K. WOŹNY[2], P. ŻABIŃSKI[1], M. WOJNICKI[1,2*]

ELECTROCHEMICAL METHOD OF COPPER POWDER SYNTHESIS ON ROTATING ELECTRODE IN THE PRESENCE OF SURFACTANTS

This paper presents a method of synthesizing copper powders by electrochemical method with the use of a rotating working electrode. The influence of the rotation speed of the working electrode, the current density, the concentration of copper ions, and the addition of ethylene glycol on the shape, size, and size distribution of the obtained powders were investigated. Properties of the synthesized powders were characterized by scanning electron microscopy (SEM) and X-ray powder diffractometry (XRD). It has been shown that it is possible to obtain copper powders with a size of 1 μm by an electrochemical method using the rotary cathode, in sulphate bath with addition of ethylene glycol as a surfactant. Increasing current density causes a decrease in the average size of the obtained powder particles. The addition of 2.5% of ethylene glycol prevents the formation of dendritic powders. The change in the concentration of copper ions in the range from 0.01 to 0.15 mol/dm^3 in the electrolyte did not show any significant effect on the size of obtained particles. However, higher concentrations of copper limiting the presence of dendritic-shape particles. Changing the speed of rotation of the electrode affects both the size and the shape of synthesized copper powder. For the rotational speed of the electrode of 115 rpm, the obtained powders have a size distribution in the range of 0-3 μm and an average particle size of 1 μm. The particles had a polygonal shape with an agglomeration tendency.

Keywords: Copper powder; electrochemical synthesis; rotating electrode; ethylene glycol

1. Introduction

Powder metallurgy is a method of producing elements made of metallic or non-metallic powders, without a liquid-solid phase transition. Fine particles of metal powder are combined into a shaped mass as a result of an annealing and pressing process in an inert or reducing atmosphere [1,2]. The process of manufacturing components made of metal powders is an economical method for fabrication of small size parts and simple shapes, as a result of which compacted elements are obtained. It is also worth mentioning the additive technology, better known as 3D printing. The process uses a laser beam to sinter the powder particles into a given shape, layer by layer. This solution does not require expensive dies and allows for the production of almost any shape. However, this application requires powders of very small size and a narrow size distribution. Particles with a size of 1 μm +/– 0.5 μm with a spherical shape are most preferred for additive technologies. [3-6].

Powders of copper and its alloys are of particular interest due to their physicochemical properties. High thermal and electrical conductivity, plasticity, and good catalytic and bactericidal properties make copper and copper alloys widely used in powder metallurgy. Currently, copper powders are produced by methods such as: atomization, chemical reduction of oxides or carbonates, and electrochemical methods [7,8].

The production of copper powders by electrochemical reduction is one of the most promising techniques. By adjusting the current parameters, electrolyte composition, and electrode material, it is possible to control the size of the obtained powders in a relatively wide range. In classical copper electrolysis, the aim is to obtain solid cathode deposits. In the case of electrochemical preparation of powders, the aim is to synthesize the powder material with the smallest possible size of single particles. Such a powder shows technical properties allowing for the production of objects with good accuracy and compaction. Moreover, the smaller the grain size of the powder, the greater the specific

[1] AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, AL. MICKIEWICZA 30, 30-059 KRAKOW, POLAND
[2] CBRTP SA RESEARCH AND DEVELOPMENT CENTER OF TECHNOLOGY FOR INDUSTRY, LUDWIKA WARYŃSKIEGO 3A, 00-645 WARSZAWA, POLAND

* Corresponding author: marekw@agh.edu.pl

surface area, which is a certain difficulty in processing due to the tendency to surface oxidation, but, on other hand it improves its catalytic and technological properties.

However, in order to obtain a powdery cathode deposit, it is necessary to maintain a high current density during the process with a low concentration of copper ions [9]. Due to the relatively low overpotential for hydrogen evolution on copper, amounting to 590 mV for the sulphate electrolyte [10] , it leads to a competitive hydrogen evolution reaction at the cathode, which reduces the current efficiency of the process. Moreover, the emitted bubbles of hydrogen negatively affect the quality of the copper powder deposit. The hydrogen evolution on the copper cathode deposit increases the porosity of the copper powder deposit. The hydrogen bubble physically blocks the access of the copper surface from the electrolyte, therefore no electrolysis takes place here. As a result, craters form where the hydrogen bubbles occur [10-12]. This increases the development of the surface of the resulting powder, making it more susceptible to oxidation. These phenomena are a serious limitation for the process.

The solution to this problem may be related to modification of the electrolyte composition or the physical parameters of the electrodeposition process. In the scientific literature, the influence of current density, electrolyte composition, and concentration [13-16] on the efficiency of the electrolysis process has been considered. It is also well known, that the temperature and mixing of the solution also affect the kinetics of chemical and electrochemical reactions, which is confirmed by a literature review [14].

An interesting idea was provided by the authors of the publication, who proposed to conduct electrolysis under a super gravitational field. Under these conditions, the concentration polarization of Cu^{2+} ions decreases and thus the current efficiency of the process increases [17].

The influence of organic additives on the electrolysis process and the quality of the obtained copper powder was also investigated, which shows that some of them allow for obtaining smaller copper particles while maintaining a relatively high current efficiency [18]. This phenomenon is commonly used in classical bulk copper electrolysis. Additives like glycerol or other polyols increase the cathode overpotential and counteract hydrogen co-evolution [19-22]. In this way, they increase the efficiency of electrolysis and make it possible to maintain a higher current density.

In the literature, mechanical improvements to the electrolytic synthesis of copper powders, such as an electrode from a rotating disk or cylinder, have also been proposed [23-26]. In this version of the process, the cathode in cylindrical shape rotates, partially immersed in the electrolyte. The cathodic reaction runs only in the part immersed in the electrolyte, while in the part not immersed in the electrolyte, the reaction theoretically stops. Thanks to this, with an appropriately selected rotational speed, it should be possible to capture and separate the powder from the cathode immediately after nucleation, before it has time to grow into much larger particles in the further stages of electrolysis. In this case, organic additives were also used.

The powder synthesis technology proposed in the work below is characterized by a hydrodynamic system. The solution we propose has a much greater impact on the diffusion and thus mass and charge transport during electrolysis compared to a static system with mixing. This may be of key importance for the quality of the obtained cathode deposits, with particular emphasis on powders. The aim of this work is to investigate the effect of cathode density, the concentration of copper ions in the electrolyte, as well as the addition of glycol and the rotational speed of the cylindrically shaped electrode on the size, shape and size distribution of the obtained copper particles.

Ultimately, the research will aim to obtain particles with a size of 1 μm +/– 0.5 μm and a spherical shape as a substrate for additive technologies.

2. Experimental

The MCP M10-SP-3020E laboratory power supply was used to power the electrolyzer. A container made of PVC, characterized by high resistance to sulfuric acid, was used as the electrolyzer tank. A stainless-steel (austenitic, grade 316) tubular electrode with an external diameter of 70 mm and a wall thickness of 2 mm was used as the rotating cathode. An aluminum rod was used to make the axes of the rotating electrode, which was mounted on graphite bearings with very good electrically conductive properties and good lubricating properties, which allowed to obtain a low resistance to rotation of the cylinder. This cathode conducts electricity well and it is resistant to the sulphuric acid. The electrolyzer constructed in this way was connected with a laboratory stirrer, which allowed for the electrode rotation. This is shown schematically in Fig. 1A-B.

An important element of the system was a rubber squeegee, which was used to remove the micropowder from the roller surface in order to prevent further grain growth (Fig. 1C).

The anode was made of 99.99% pure copper. Unless otherwise stated, the electrolyte contained 0.5 mol/dm^3 H_2SO_4 (p.a., Chempur 95%). The effect of surfactants was tested. For this purpose, ethylene glycol (p.a., Chempur 99,9%) was added to the bath in selected experiments. Some copper sulfate was also added to the electrolyte. Unless otherwise stated, this content was 0.15 mol/dm^3 and the rotational speed was variable in the range from 0 to 201 RPM. The effect of the cathode current density for three current densities was investigated for 0.26; 0.39, and 0.52 A/cm^2. The duration of the electrolysis was 300 s in each case.

In order to determine the current density, it was necessary to calculate the surface area of the electrode immersed in the electrolyte and the immersion time of a given cathode point. Knowing the diameter of the cylinder and the immersion depth, it is possible to calculate the surface area of the electrode in the electrolyte (Fig. 1D). It was calculated that the surface area of the electrode immersed in the electrolyte was 38.0 cm^2. The surface area of the anode was 38.5 cm^2.

To determine the actual duration of the electrolysis, it is necessary to calculate the residence time of the theoretical elec-

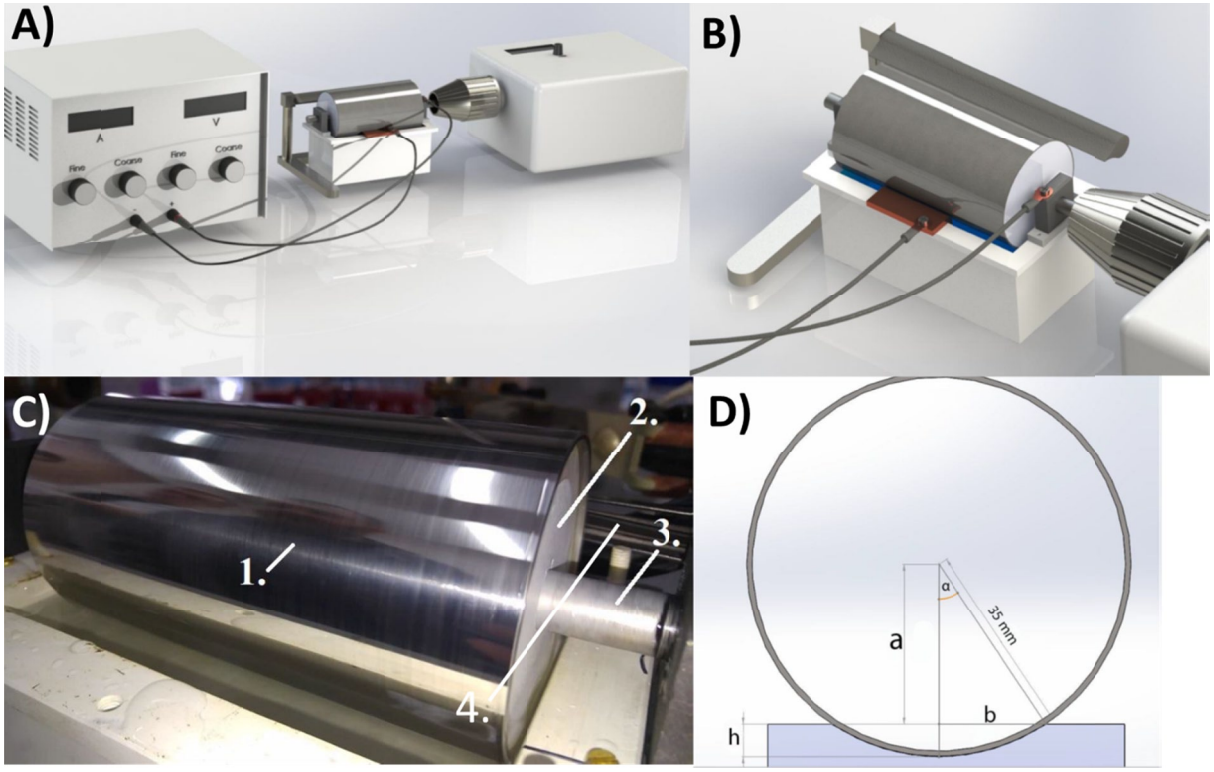

Fig. 1. A) View of the experimental setup, B) working electrode, C) working electrode 1. SS316 surface, 2. PTFE sealing, 3 aluminum rod – supplying electricity to the working electrode, 4. welt – to remove products from electrode, D) geometry of the electrode cross-section

trode point moving in the electrolyte. Knowing the arc length of the cylinder immersed in the electrode (29.2 mm), it can be calculated that for the rotational speed of 115 rpm, the time during which a given point of the electrode will be immersed in the electrolyte is 0.069 s. After this time, the electrolysis will be interrupted and the obtained cathode deposit will be collected by the mounted scraper, followed by subsequent rotation of the electrode roller.

The particle size and shape of the powders obtained were examined with a SU-70 scanning electron microscope. The particle size measurement was carried out in accordance to the PN-84 / H-04956 standard (EUR 20268 EN). The particle crystallography was investigated by XRD Rigaku. Image analysis was performed in ImageJ software.

3. Results

3.1. The influence of current density on the particles size

Fig. 2. shows that increasing current density from 0.26 to 0.52 A/cm^2 has significant impact on average particle size of the obtained cathodic deposit. Moreover, if we consider the particle size distribution of each powder, it can be noticed that contribution of different particle sizes changes significantly on the influence of different current density. For the sample obtained with a current density of 0.26 A/cm^2 the size of the powders ranges from 0.5 to 6.5 µm. About 70% of the powders are between 1.5 µm and 3.5 µm in size. In the range of 1 µm (+/– 0.5 µm) we are the most interested in, only 16% of the produced powders is received. The copper powder obtained at the cathodic current density of 0.39 A/cm^2 has an average particle size ranging from 0.5 to 6.5 µm. Approximately 34% of the produced powder is in the range of 0.5 µm to 1.5 µm. For a current density of 0.52 A/cm^2, the particle size is in the range of 0.5 to 2.5 µm, with as much as 80% in the range of 0.5 to 1.5 µm.

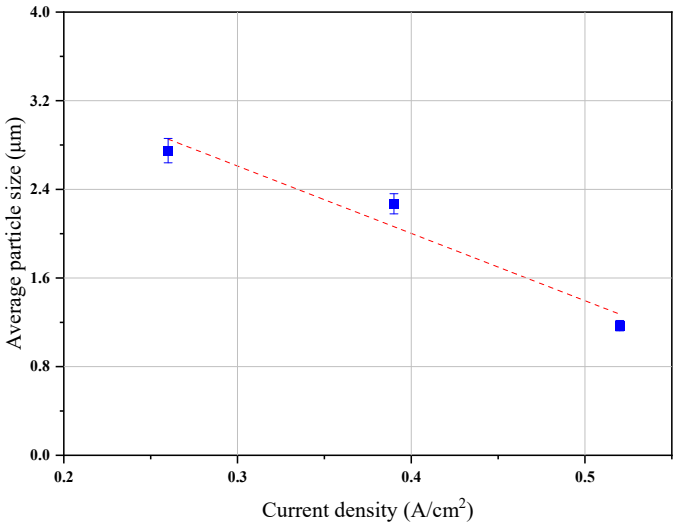

Fig. 2 Effect of current density on the average size of the obtained copper powder particles. The current density was 0.26; 0.39, and 0.52 A/cm^2. The cathode rotational speed was 115 RPM, the copper concentration in the electrolyte was 0.15 mol/dm^3. The electrolyte contained 2.5% vol. ethylene glycol. The duration of the electrolysis was 300sec

In order to determine the shape of the obtained copper particles, SEM micrograph was performed for each sample (micrographs not included in the manuscript). Regardless of the current density, the particles in every sample show a polyhedral shape and form agglomerates.

3.2. The influence of addition of surfactants on particles size

To determine the effect of surfactant on the quality of copper cathode deposits formed during electrolysis, a series of experiments using ethylene glycol were carried out.

The copper ions concentration in the electrolyte was 0.1 mol/dm^3. Concentrated sulfuric acid (VI) was also added to the solution in the amount of 0.5 mol/dm^3. The duration of the process was 300 s and the rotational speed of the cathode was 115 rpm.

The experiments were carried out for the same current densities as in the previous point: 0.26; 0.39; 0.52 A/cm^2 in the version with the addition of 25 cm^3 of glycol per 1 dm^3 electrolyte and in the version without this additive.

As shown in Fig. 3 and Fig. 4 the influence of the addition of ethylene glycol on the average size of the obtained copper particles is significant. For each current density used, the average powder size in the glycol series was smaller than in the non-glycol series. This relationship is clearly visible on the attached trend lines.

For the experimental series carried out for a current density of 0.26 A/cm^2, the particle size of the copper powder is in the range from 0.5 to 5.5 µm (Fig. 4). Slightly over 30% of powders have a size from 0.5 to 1 µm. With the same current density, but with the addition of 25 cm^3 of ethylene glycol, already more than 65% of the measured particles are within this range (Fig. 4).

There is also a dependence of the shape of the obtained copper particles on the presence of a surfactant. The SEM test shows that the particles obtained with the method without glycol have a dendritic shape and are loosely bound together (Fig. 5).

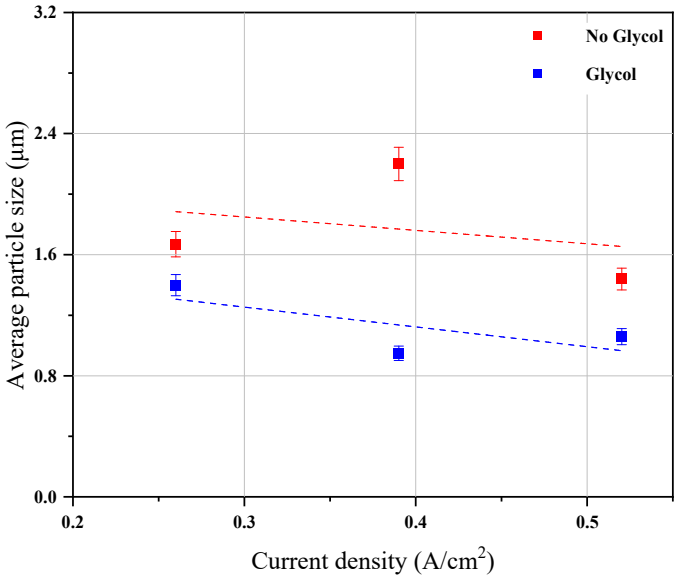

Fig. 3. Influence of the addition of ethylene glycol on the average size of the obtained copper powder particles for different current densities. The current density was 0.26; 0.39, and 0.52 A / cm^2. The cathode rotational speed was 115 RPM, the copper concentration in the electrolyte was 0.1 mol/ dm^3. The duration of the electrolysis was 300sec

On the other hand, the addition of glycol to the process produces agglomerates of particles with a polyhedral shape.

Increasing the current density during the process to 0.39 A/cm^2 leads to an increase in the particle size distribution for a process conducted without glycol (histograms not included in the manuscript). The grain size of the powder obtained in the experiment with the addition of glycol is in the range from 0.5 to 3 µm (Fig. 6). About 65% of the measured particles are between 0.5 and 1.5 µm, although, there are also particles larger than 9 µm. The powders obtained in this experiment are mostly flake-shaped, but among them there are also particles having a polyhedral and granular shape.

The addition of glycol to electrodeposition at the current density 0.39 A/cm^2 leads to a significant reduction in particle

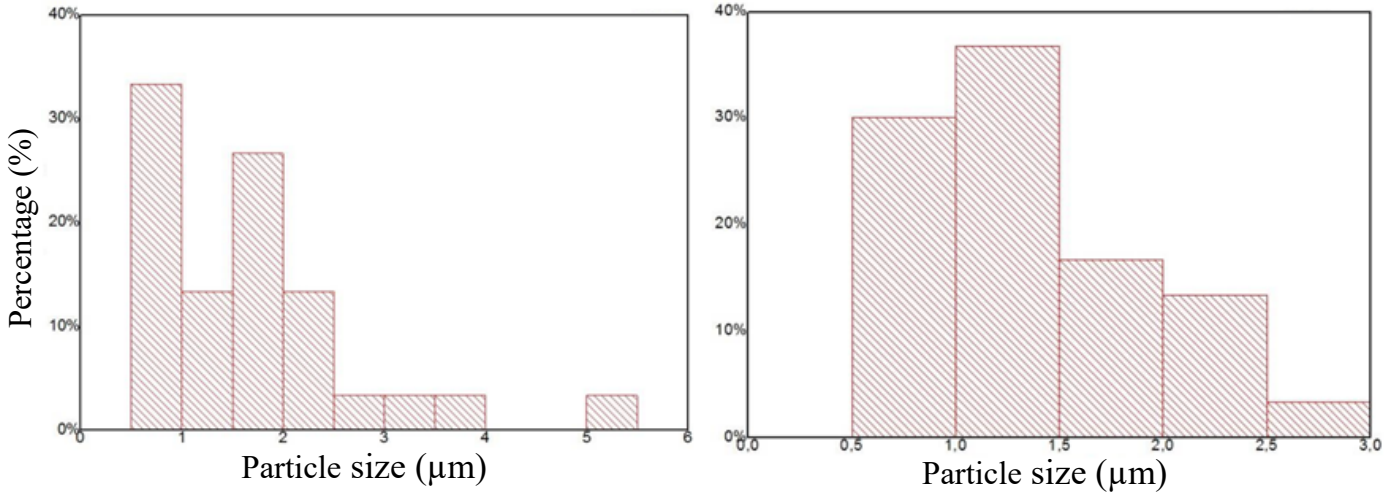

Fig. 4. Grain size distribution: 0.26 A/cm^2, no added glycol (left), 0.26 A/cm^2, with addition of 2.5% vol. glycol (right). The cathode rotational speed was 115 RPM, the copper concentration in the electrolyte was 0.1 mol/dm^3. The duration of the electrolysis was 300sec

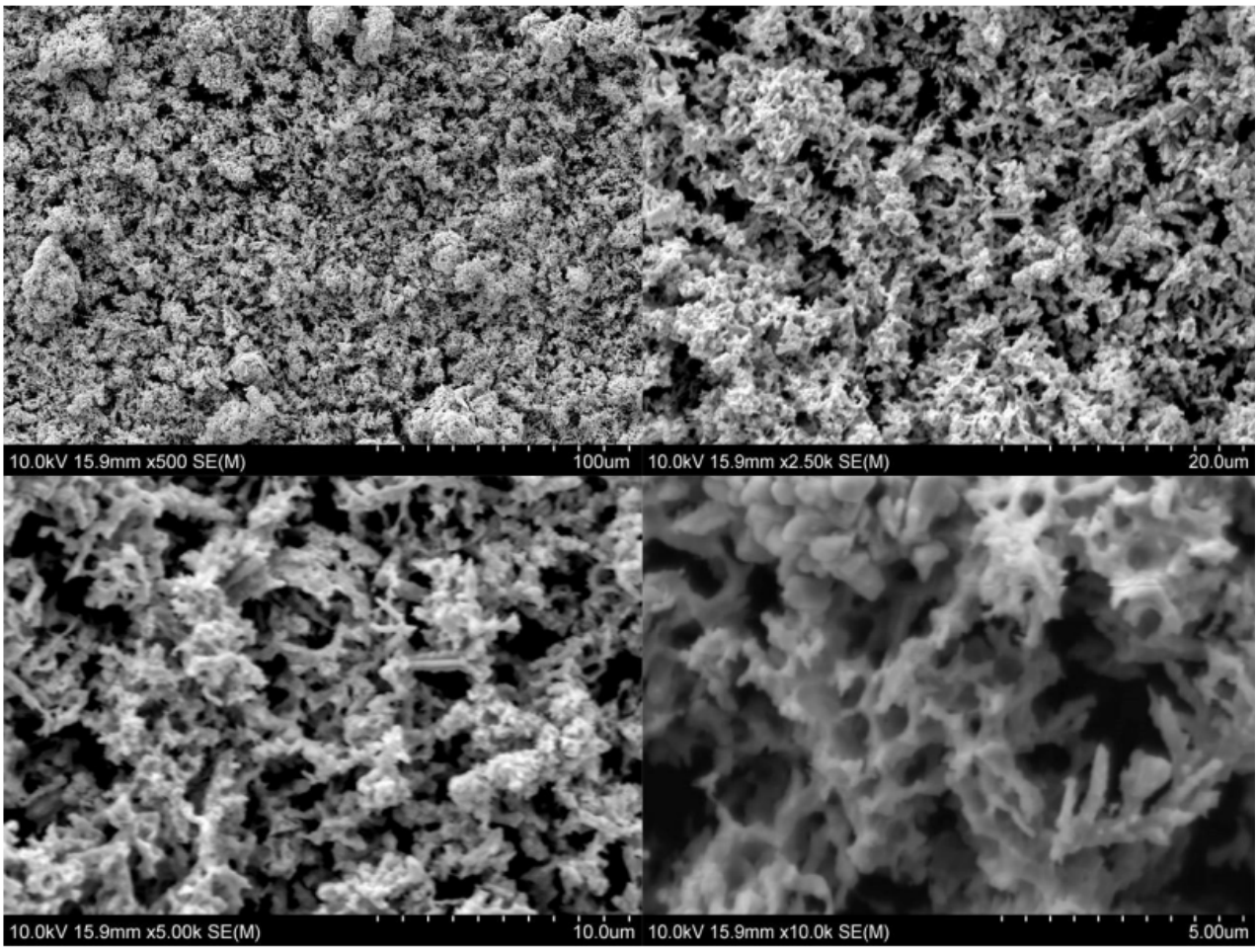

Fig. 5. SEM micrographs of copper powder obtained at 0.26 A/cm^2, without addition of ethylene glycol. The cathode rotational speed was 115 RPM, the copper concentration in the electrolyte was 0.1 mol/dm^3. The duration of the electrolysis was 300sec

size. About 8% of the powder is less than 0.5 µm. As much as 88% of particles in the obtained powder, is within the size range from 0.5 µm to 1.5 µm. The particles obtained under these conditions have a polyhedral shape and a strong tendency to agglomerate (Fig. 6).

The powders obtained with the electrolyte with copper concentration of 0.01 mol/dm^3, current density 0.29 A/cm^2, without the addition of ethylene glycol, were analyzed using the XRD method. The obtained results are presented in Fig. 7.

From the obtained results we can differentiate the diffraction peaks corresponding to the metallic copper Cu (111), Cu (200) and Cu (220) respectively. By the identification of CuO (111) and CuO (202) peaks, the presence of the copper oxide has been confirmed. Using the Scherrer equation (1), the grain size was calculated (TABLE 1).

$$d = \frac{k * \lambda}{\beta * \cos\theta} \tag{1}$$

where: d – particle size in nm, K_α – 0.94; λ – 0.1541 nm; β – half-width of the peak, cosθ – position of the highest point of the peak, given in degrees.

If a particle size obtained from the SEM analysis coincides with the particle size value obtained from the XRD analysis, it

TABLE 1

Grain size obtained from XRD analysis of copper powder synthesized with the electrolyte with copper concentration of 0.01 mol/dm^3, current density 0.29 A/cm^2, without addition of ethylene glycol

CuO(002)	CuO(111)	Cu(111)	Cu(200)	CuO($20\bar{2}$)	Cu(202)
0.90 [µm]	1.06 [µm]	0.83 [µm]	0.25 [µm]	0.37 [µm]	0.3 [µm]

may suggest that these particles are monocrystalline. The average particle size obtained from SEM analysis equals 0.99 µm and the average crystalline size obtained from the Scherrer's equation was equal to 0.74 µm (σ = 0.39 µm). Comparing the results, one can conclude that a large fraction of obtained powders is monocrystalline. Despite the similarity of these results and the characteristic shape of the obtained particles, it cannot be unequivocally stated that they are monocrystalline particles, due to the fact, that Scherrer's equation does not show sufficient accuracy for such a large crystalline size. What is more, such an analysis is difficult in this case, due to the relatively wide distribution of particle size. This issue requires further research using more sophisticated methods.

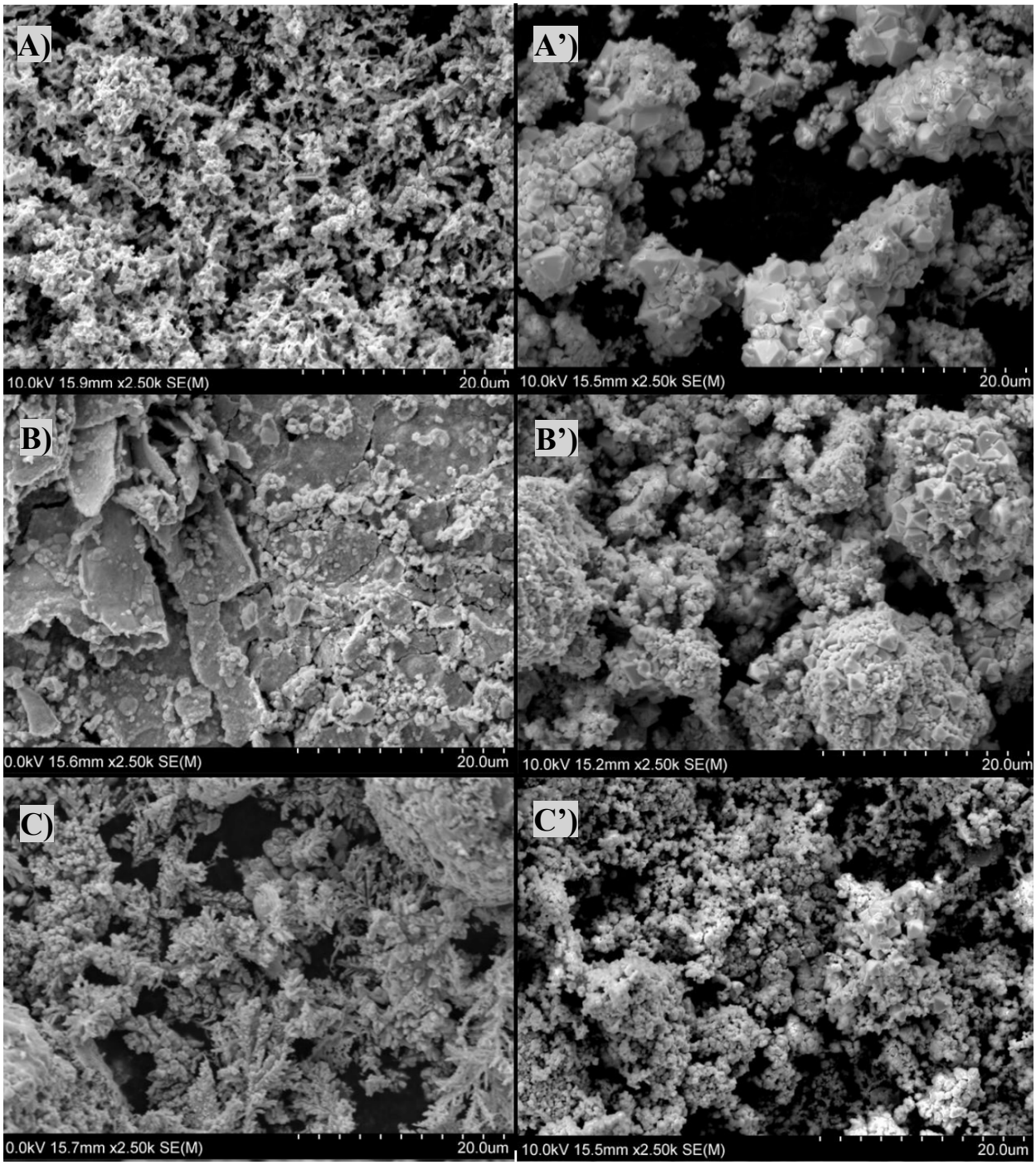

Fig. 6. SEM micrographs of copper powder obtained at: A) 0.26 A/cm^2 without addition of ethylene glycol, A') 0.26 A/cm^2, with addition of 2.5% vol. ethylene glycol, B) 0.39 A/cm^2 without addition of ethylene glycol, B') 0.39 A/cm^2 with addition of 2.5% vol. ethylene glycol, C) 0.52 A/cm^2 without addition of ethylene glycol, C') 0.52 A/cm^2 with addition of 2.5% vol. ethylene glycol. The cathode rotational speed was 115 RPM, the copper concentration in the electrolyte was 0.1 mol/dm^3. The duration of the electrolysis was 300sec

3.3. The influence of copper (II) ions concentration on the particles size and shape

In order to investigate the influence of the concentration of copper ions on the size and shape of the synthesized copper powders, a series of experiments was carried out for the concentration of copper ions in the electrolyte in the amount of: 0.01 mol/dm^3; 0.05 mol/dm^3; 0.075 mol/dm^3; 0.15 mol/dm^3.

Concentrated sulfuric acid (VI) was also added to the solution in the amount of 0.5 mol/dm^3. The duration of the process was 300 s and the rotational speed of the cathode was 115 rpm. Current density was 0.52 A/cm^2 for each experiment. All experiments were carried out with the addition of ethylene glycol in the amount of 25 cm^3 per liter of solution.

As can be observed in Fig. 8 the concentration of copper ions in the tested range have almost no influence on the average particle size of the obtained copper powders.

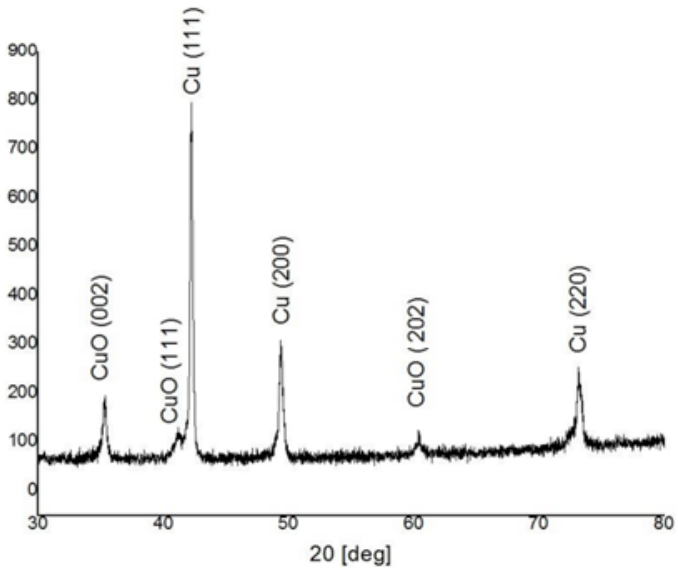

Fig. 7. XRD pattern of copper powder synthesized with the electrolyte with copper concentration of 0.01 mol/ dm^3, current density 0.29 A/ cm^2, without addition of ethylene glycol

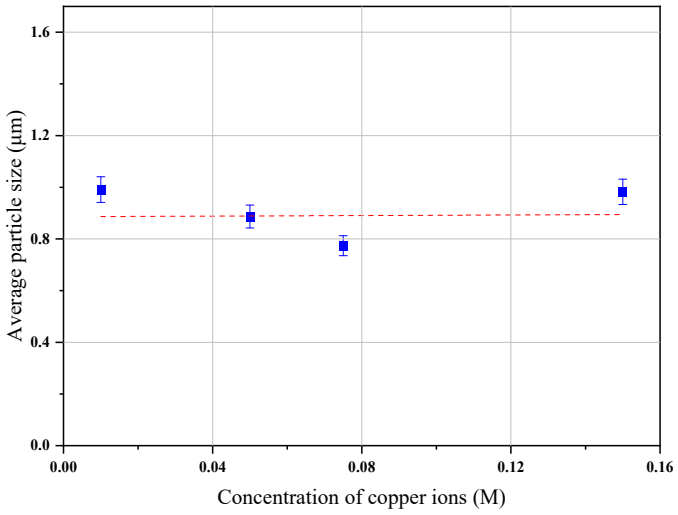

Fig. 8. Effect of concentration of copper ions in the electrolyte, on the average size of the obtained copper powder particles. The cathode rotational speed was 115 RPM, the concentration of copper ions in the electrolyte in the amount of: 0.01 mol/dm^3; 0.05 mol/dm^3; 0.075 mol/dm^3; 0.15 mol/dm^3. The duration of the electrolysis was 300sec. Current density was 0.52 A/cm^2. The electrolyte contained 2.5% vol. ethylene glycol

This is probably due to the fact that the rotational movement of the electrode eliminates or strongly limits the phenomenon of the stationary layer at the electrode surface. For this reason, the process is not in the area of diffusion control. SEM analysis showed, however, that the concentration of copper in the electrolyte influences the particles shape.

The conducted experiments have shown that the lowest studied concentration of copper (II) ions in the electrolyte (0.01 mol/dm^3) allows obtaining homogeneous powders. The particles are multi-sided and their surface is smooth and free from fraying. However, they tend to agglomerate. The particle size distribution of the obtained powder is in the range of 0-3 µm. Percentage of particles with a size 0.5 ± 1 µm is over 65%.

Increasing the electrolyte concentration to 0.05 mol/dm^3 caused a significant change in the shape and size of the obtained powders compared to the concentration of 0.01 mol/dm^3. The most common there are dendritic-shaped particles. There are also coniferous / fibrous particles. Some of them are clumped together. Obtained powders are in the range from 0 to 2.5 µm. About 65% of them are below 1 µm. Particles from 0.5 to 1.0 µm have the largest share and it approaches 45%. Particles with a size of 1 ± 0.5 µm represents approx. 65%.

When using an electrolyte with a copper concentration of 0.075 mol/dm^3, the obtained particles have a polyhedral, fragmented shape, and only a few of them are globular. As with lower concentrations, the particles stick together and form agglomerates. The vast majority of the measured particles are up to 0.5 µm. Only 23% are larger than 0.5 µm. The particle size distribution is irregular in the range between 0 and 4.5 µm.

The use of an electrolyte with a copper concentration of 0.15 mol/dm^3 made it possible to obtain powders of a polyhedral shape. No other shape was observed. The particles form expanded agglomerates. The most common size range is 0.5-1 µm, which is 73%. At this electrolyte concentration, the obtained particles are in the range of 0-2.5 µm.

3.4. Electrode rotation speed

A series of experiments with different rotational speeds of the electrode was carried out. In each case, the concentration of copper ions in the electrolyte was 0.01 mol/dm^3, and the current density was 0.52 A/cm^2. As in the previous experiments, 0.5 mol/dm^3 sulfuric acid was in the electrolyte bath. All series of experiments were carried out with the addition of ethylene glycol in the amount of 25 cm^3 per liter of solution. The duration of each cycle was 300 s.

Under these conditions, a series of experiments were carried out for the rotational speeds of the cylindrical electrode, respectively: 0; 39, 115, 162, 201 RPM.

Fig. 9 shows the average particle sizes of the powders from the performed syntheses. The dependence on the rotational speed of the electrode has a more complicated model here. The plot line shows oscillations, but the trend line attached in the figure suggests that with the increase in rotational speed, the average size of the obtained copper powders decreases.

In the first case, the powders obtained from electrolysis without cylinder rotation were considered. This is to compare how the morphology of the powders changes as a result of the increase in the speed of rotation to the powders obtained without the use of a rotating electrode. SEM analysis (Fig. 10) showed that, in the absence of rotation, the obtained powders have mainly a polyhedral shape and to some extent a dendritic shape. There was a tendency to agglomerate. The particle size ranges from 0.5 to 6.5 µm, however, powders larger than 4 µm are a significant minority. The largest number (about 27%) of powder particles

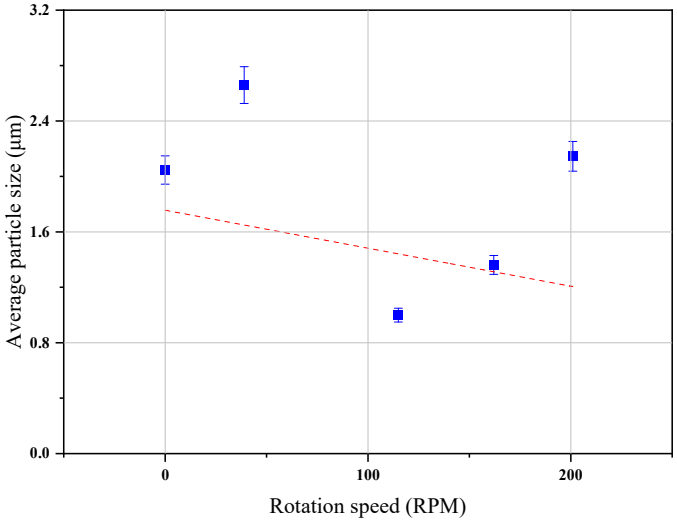

Fig. 9. Effect of rotation speed of electrode on the average size of the obtained copper powder particles

is from 2 to 2.5 µm. The grain size of 1 ± 0.5 µm is only a share of the order of 20%.

The current density was 0.52 A/cm^2. The cathode rotational speed was 0; 39, 115, 162, 201 RPM, the copper concentration in the electrolyte was 0.01 mol/dm^3. The duration of the electrolysis was 300sec. The electrolyte contained 2.5% vol. ethylene glycol.

When the rotation of the electrode at 39 rpm during electrolysis was used, the shape and size of the particles changed. The tendency to agglomerate has been observed (Fig. 12A). An increase in the number of dendritic-shaped particles was observed at the expense of polyhedral-shaped particles in relation to electrolysis without rotation. The analysis of the empirical distribution showed that the particles have a size in the range from 0.5 to 6.0 µm. Particles with a size of 1 ± 0.5 µm occur more often than in experiment without rotation, but still only the content of the order of 30%. Most of the tested particles from the obtained powder were in the size range of 1 to 1.5 µm.

After increasing the speed of the electrode to 115 rpm, it results that the particles of dendritic shape practically do not occur. The vast majority are particles with a polyhedral shape (Fig. 12B). The surface of the tested particles is smooth and regular, no other shapes were observed. The powders form dilated agglomerates. The obtained particles had a size in the range of 0 to 3 µm. The distribution is narrow and the most common result is grain sizes between 0.5 and 1.0 µm, which is approximately 45%. Particles with a size in the range of 1 ± 0.5 µm are in amount over 65%. The particles larger than 1.5 µm in total constitute about 15% (Fig. 11).

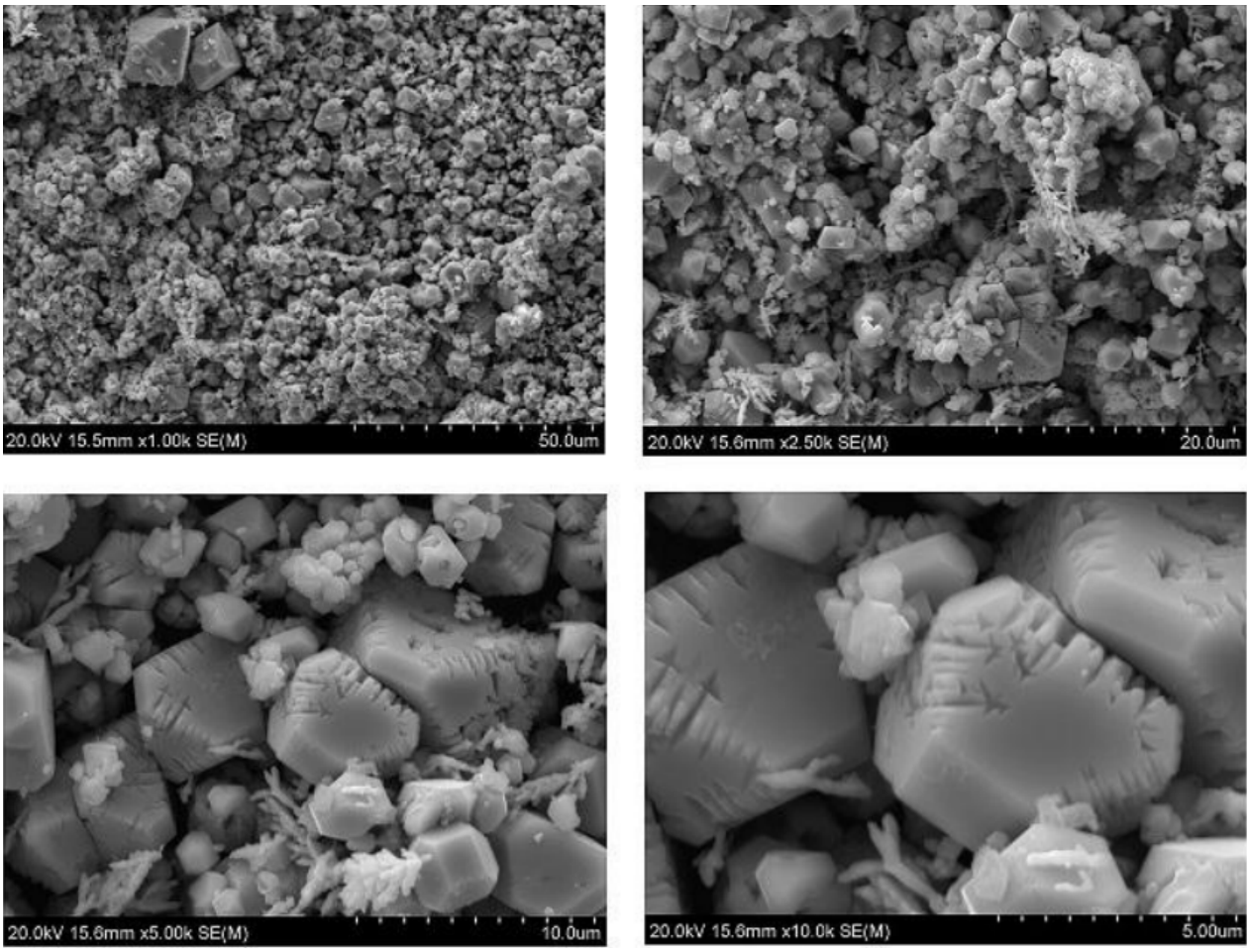

Fig. 10. SEM micrographs of copper powder obtained at 0.52 A/cm^2, without electrode rotation. The copper concentration in the electrolyte was 0.01 mol/dm^3. The duration of the electrolysis was 300sec. The electrolyte contained 2.5% vol. ethylene glycol

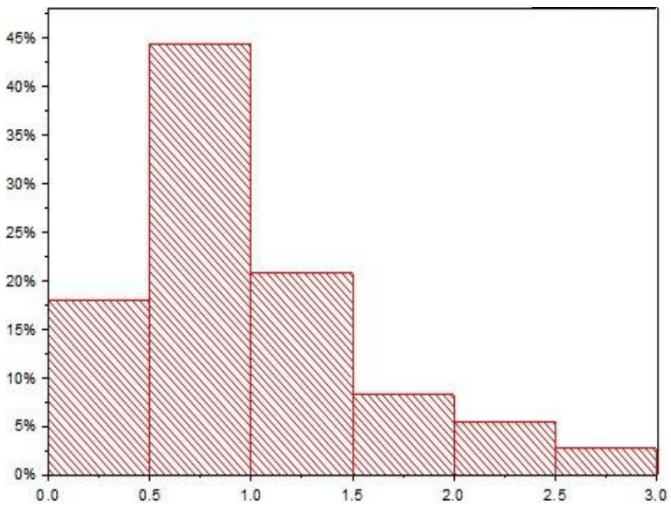

Fig. 11. Grain size distribution. (0.52 A/cm^2, with electrode rotation 115RPM). The copper concentration in the electrolyte was 0.01 mol/dm^3. The duration of the electrolysis was 300sec. The electrolyte contained 2.5% vol. ethylene glycol

At 162 rpm of the cylinder, the obtained particles have a polyhedral and fragmented shape. Also, particles with globular shape begin to appear (Fig. 12C). As in the previous cases, the particles clump into larger clusters, but it is not as noticeable as when the cathode was rotating at 115 rpm. Increasing the cathode rotational speed to 162 rpm causes the size distribution to shift towards higher values. There are practically no particles in the size range from 0 to 0.5 µm (below 3%). The most common size is between 1 and 1.5 µm. The percentage of powders with a size in the range of 1 ± 0.5 µm is almost 65%.

The powder obtained at the speed of 201 rpm is characterized by the dominance of the dendritic shape. There are also small amounts of particles with polyhedral, globular and fragmentation shapes. The particles stick together in medium-sized clusters (Fig. 12D).

The largest particles occurring are up to 5 µm. Wide distribution of sizes. Powders in the 1 and 1.5 µm range are all below 25%. The largest number of particles from the tested sample was in the range of 2.5 to 3.0 µm.

4. Discussion

The aim of this study was to obtain copper powders with a size of 1 µm within the size distribution range of +/– 0.5 µm. This size of copper powder particles was chosen due to its potential application in 3D printing pastes. The novelty of this paper is based on the usage of a rotating cylinder cathode instead of

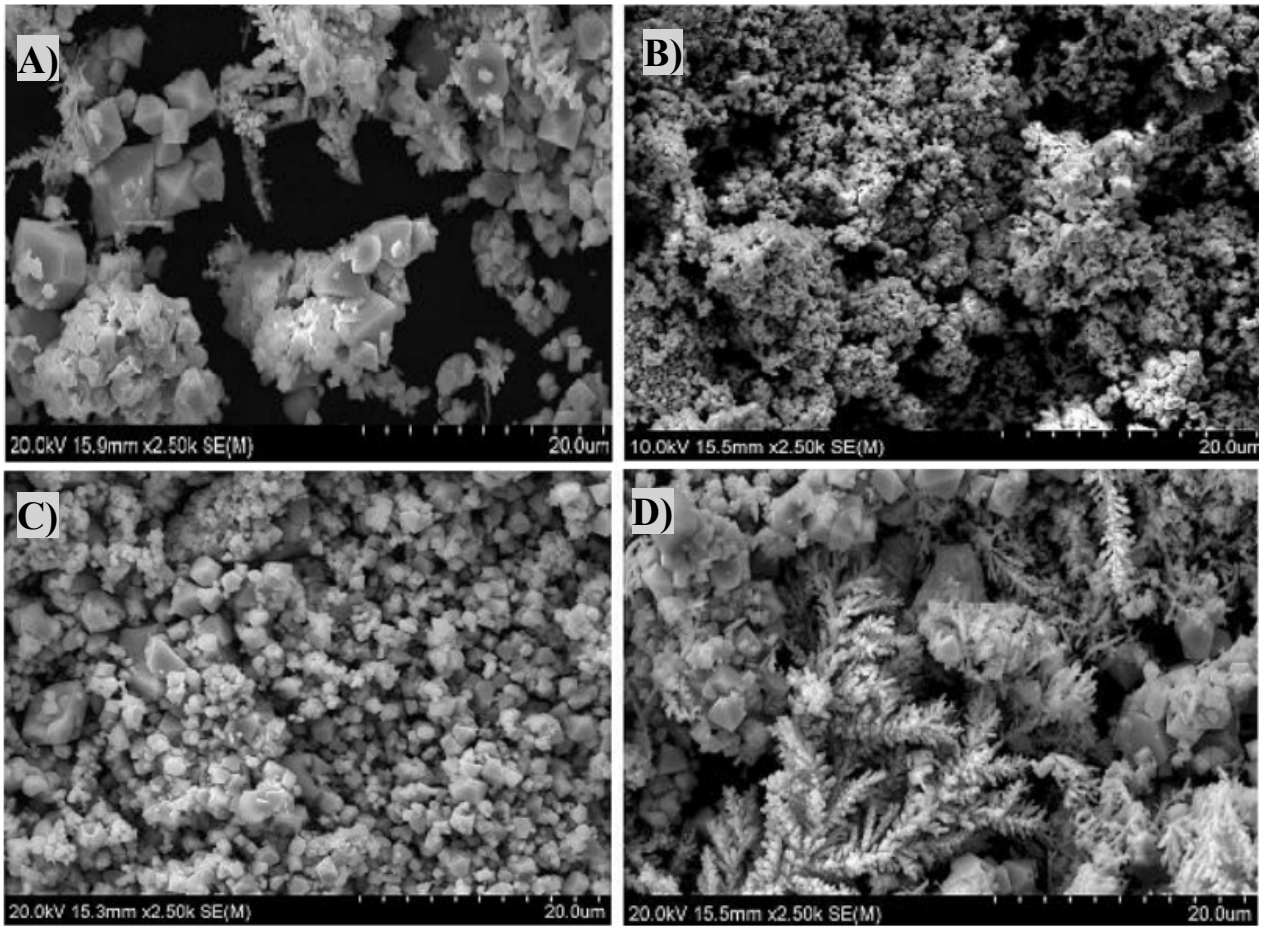

Fig. 12. SEM microphotography of copper powder obtained at 0.52 A/cm^2, with electrode rotation: A) 39RPM; B) 115RPM; C) 162RPM; D) 201RPM. The copper concentration in the electrolyte was 0.01 mol/dm^3. The duration of the electrolysis was 300sec. The electrolyte contained 2.5% vol. ethylene glycol

a disc [27,28]. The main advantage of this solution is the same speed of rotation at every point of the warking electrode (this property is used in corrosion studies [29,30]), whereas, in the disc-shaped electrode, the rotating speed depends on the distance from the center of the electrode. Such gradient could lead to the biger particles size distribtuion.

The study proved that it is possible to obtain powders with a size of approx. 1 μm in the process of electrolytic copper deposition with the use of a rotating electrode in the area of limiting currents. This assumption was based on the observation of oxygen evolution reaction on the surface of the copper anode. Consequently, the process was under diffusion control [31]. To prevent this phenomenon, we propose adding a second anode to increase the anode reaction surface.

The conducted tests have shown that the shape and size of the powder are influenced by parameters such as the current density of electrolysis, the addition of surfactants, and the speed of electrode rotation. However, the change in the concentration of copper ions in the electrolyte did not show any significant effect on the size of obtained particles in the concentration range used.

The first part of the experiment was to determine the effect of electrolysis current density on the morphology and size distribution of the resulting powders. Analyzing the above results, it can be concluded that with the increase of the current density, the average size of the obtained powders decreases, which could be referenced in the study of G. Orhan et al. [33]. However, in our case shape of obtained particles remains unchanged in the studied spectrum of current densities.

The aim of the second part of the experiment was to investigate the influence of a surfactant, in this case, ethylene glycol, on the morphology and size distribution of the obtained powders. After analyzing the results of the research, it can be concluded that the addition of a small amount of ethylene glycol to the electrolyte has a significant impact on the shape of the obtained powders. Moreover, it has been shown that this phenomenon works synergistically with the change of the current density. For each of the applied current densities, smaller average size of the powders in the system with the addition of glycol was obtained, while smaller powders were obtained for higher current densities. The percentage of ethylene glycol in the electrolyte was 2.5%.

The experiment proved that the addition of the surfactant prevents the formation of dendrite-shaped powder deposits. During the experiment, a reduction in the surface tension of the electrolyte was also noticed, which prevented the powders from floating on the electrolyte surface. The addition of glycol could, however, promote the formation of agglomerates of the synthesized powders.

In the case of the experiment carried out at a current density of 0.39 A/cm^2 without the addition of ethylene glycol, a significant change in the shape of the obtained powder was noticed. A major part of the produced particles had a flake shape and the average grain size was the largest in the series. The literature reports that the use of surfactants in rotating cylinder electrodes allows the synthesis of small particles, however, it tends to create agglomerates from synthesized particles [25]

During the experiments, a significant increase in the temperature of the electrolyte and electrodes caused by the current flow was noticed. This certainly has a direct impact on both the size and shape of the powders obtained. Another phenomenon that can affect the shape of the received powders, the cathode surface becomes tarnished due to the application of sulfuric acid containing electrolyte and the elevated temperature.

To exclude the influence of these phenomena on the results, in future studies, the electrolytic cell will be thermostated with a Peltier cell, while the electrode will be made of stainless steel with higher corrosion resistance.

In the next part of the work, the influence of the concentration of copper ions in the electrolyte on the quality of the obtained copper powders was investigated.

The analysis of the obtained results showed that increasing the concentration in the range from 0.01 to 0.15 mol/dm^3 did not reduce the size of the powder, as it is observed for the electrolysis in the reactor without agitation. This is probably due to the rotation of the cylindrical electrode, which limits the phenomenon of diffusion control. However, it is not completely eliminated, because the change in the concentration of copper ions affects the shape of the obtained powders. The use of the lowest considered concentration allows for obtaining powders with a polyhedral shape. The concentration of 0.05 mol/dm^3 causes the increase in the amount of dendritic particles and a significant decrease in the number of particles of a different shape, which is consistent with the study of M.G. Pavlov et al. [32], which uses a rotating disc electrode. However in our case, further increasing the electrolyte concentration eliminated the presence of dendrites. These phenomena could be caused by the usage of a rotating cylinder electrode instead of a disc.

At 0.075 mol/dm^3, globular and fragmented particles are noticeable, which was not observed with the electrolyte with a concentration of 0.15 mol/dm^3. The highest concentration gives the homogeneous particles shape.

In the last part of the work, the influence of the rotational speed of the electrode during the synthesis on the shape and size of the obtained powders was investigated.

The conducted analysis showed a tendency to obtain smaller grain diameters, starting from 0 to 115 rpm. The median size of the particles obtained in the absence of rotation is 2-2.5 μm, at 39 rpm it is a value in the range of 1-1.5 μm, and for 115 rpm it is in the range of 0.5-1 μm. After increasing the rotational speed to 162 rpm, the median increase to the range of 1-1.5 μm can be seen, while at 201 rpm, this value is 2.5-3 μm. The attached trend line indicates that increasing the rotational speed, as could be expected, results in a smaller particle size of the copper powder. However, this impact is relatively low.

Lack of rotation of the electrode resulted in obtaining powders with a polyhedral shape and with single dendrites. Increasing the speed to 39 rpm caused the expansion of dendrites at the expense of polyhedral particles. However, at 115 and 162 rpm, the occurrence of dendritic powders disappears, and the vast majority of particles in the sample are polyhedral particles. The use of a speed of 201 rpm causes a significant growth of dendrites.

The non-linear dependence of the size of the obtained powders on the speed of rotation of the electrode may be caused by the disturbance of the assumed electrolysis mechanism, by inaccurate stripping of the copper powders with the applied stripper. Some of the powder was not removed and was subjected to further growth in the subsequent electrolysis cycles. The phenomenon was additionally intensified by the capillary dragging of the electrolyte on the electrode surface above the surface of the electrolyte. As a result, the duration of the electrolysis for the point on the electrode was significantly more than 0.069 s calculated for the example of 115 rpm. To prevent this in further research, the construction of the powder stripper should be improved, by adding a presser.

5. Conclusion

The conducted research showed that it is possible to obtain copper micro-powders with a grain size of 1 µm in the process of electrolytic copper deposition. It has been proven that as the current density increases, the average grain size of the obtained powder decreases. The addition of ethylene glycol has a significant influence on the shape and size of the obtained powders.

Increasing the concentration of copper ions in the electrolyte in the range of 0.01 mol/dm^3 to 0.075 mol/dm^3 causes a decrease in the size of the powder. It was also shown that changing the speed of rotation of the electrode changes both their size and shape.

Acknowledgment

This work was supported by project from Intelligent Development Operational Program 2014-2020, co-financed by the European Regional Development Fund, project No. POIR.01.01.01-00-1246/20-00.

Declaration of Competing Interest

The authors declare no conflict/competing of interest.

REFERENCES

[1] W. James, Powder Metallurgy Methods and Applications, Powder Metall., pp. 9-19 (2015).

[2] G. Manohar, A. Dey, K.M. Pandey, S.R. Maity, AIP Conference Proceedings **1952**, 020041 (2018).

[3] M. Seifi, A. Salem, J. Beuth, O. Harrysson, J.J. Lewandowski, Overview of Materials Qualification Needs for Metal Additive Manufacturing, JOM. **68**, 747-764 (2016).

[4] W.J. Sames, F.A. List, S. Pannala, R.R. Dehoff, S.S. Babu, The metallurgy and processing science of metal additive manufacturing, IMR. **61**, 315-360 (2016).

[5] W.E. Frazier, Metal Additive Manufacturing. A Review, J. Mater. Eng. Perform. **23**, 1917-1928 (2014).

[6] A. Bandyopadhyay, Y. Zhang, S. Bose, Recent developments in metal additive manufacturing, Curr. Opin. Chem. **28**, 96-104 (2020).

[7] S. Wahyudi, S. Soepriyanto, M.Z. Mubarok, Sutarno, Synthesis and Applications of Copper Nanopowder – A Review, IOP Conference Series: Materials Science and Engineering **395**, 012014 (2018).

[8] G.A. Mowbray, Production Methods for Powders of Copper and Copper Alloys: A Critical Review, Powder Metall. **29**, 105-107 (1986).

[9] K.I. Popov, M.G. Pavlović, Electrodeposition of Metal Powders with Controlled Particle Grain Size and Morphology, in: R.E. White, B.E. Conway, J.O.M. Bockris (Eds.) Modern Aspects of Electrochemistry: Volume 24, Springer US, New York, NY, 1993, pp. 299-391.

[10] K. Popov, S. Djokić, N. Nikolić, V. Jovic, Electrodeposition of Metals with Hydrogen Evolution, 2016.

[11] N.D. Nikolić, K.I. Popov, L.J. Pavlović, M.G. Pavlović, The effect of hydrogen codeposition on the morphology of copper electrodeposits. I. The concept of effective overpotential, J. J. Electroanal. Chem. **588**, 88-98 (2006).

[12] H.-C. Shin, J. Dong, M. Liu, Nanoporous Structures Prepared by an Electrochemical Deposition Process, Adv. Mater. **15**, 1610-1614 (2003).

[13] A.H. Abbar, Electrolytic preparation of copper powder with particle size less than 63µm, Al-Qadisiya J. Eng. Sci. **1**, 1, 32 (2008).

[14] E. Akbarzadeh, S.E. Shakib, Comparison of effective parameters for copper powder production via electrorefining and electrowinning cells and improvement using DOE methods, Int. J. Miner. Metall. **18**, 731-740 (2011).

[15] R.K. Nekouei, F. Rashchi, A. Ravanbakhsh, Copper nanopowder synthesis by electrolysis method in nitrate and sulfate solutions, Powder Technol. **250**, 91-96 (2013).

[16] S. Abbas Jasim, S. Abd Al-kadhum Mohsin, M. Ammory Jaafer, Production of Copper Powder from Ores by Elecrodeposition Process, J. Univ. Babylon Eng. Sci. **27**, 233-241 (2019).

[17] M.-y. Wang, Z. Wang, Z.-c. Guo, Preparation of electrolytic copper powders with high current efficiency enhanced by super gravity field and its mechanism, T. Nonferr. Metal. Soc. **20**, 1154-1160 (2010).

[18] W. He, X.-c. Duan, L. Zhu, Characterization of ultrafine copper powder prepared by novel electrodeposition method, J. Cent. South Univ. **16**, 708-712 (2009).

[19] J. Hu, Q. Li, M. An, J. Zhang, P. Yang, Influence of Glycerol on Copper Electrodeposition from Pyrophosphate Bath: Nucleation Mechanism and Performance Characterization, J. Electrochem. Soc. **165**, D584-D594 (2018).

[20] R.S. Barbosa, G.Y. Koga, M.L.F. Nascimento, C.A.C.d. Souza, Effect of Glycerol Addition on Copper Electrodeposition on Steel Substrate Mater. Res. **25**, (2022).

[21] P. Sivasakthi, R. Sekar, G.N.K. Ramesh Bapu, Electrodeposition and characterisation of copper deposited from cyanide-free alkaline glycerol complex bath, Transactions of the IMF **93**, 32-37 (2015).

[22] C. Lin, J. Hu, J. Zhang, P. Yang, X. Kong, G. Han, Q. Li, M. An, A comparative investigation of the effects of some alcohols on copper electrodeposition from pyrophosphate bath, Surf. Interfaces. **22**, 100804 (2021).

[23] H. Soliman, A.A. El-Moneim, Electrowinning of Copper Using Rotating Cylinder Electrode Utilizing Lead Anode, Eng. J. **03** (04), 4 (2011).

[24] C. Fabian, M.J. Ridd, M. Sheehan, Rotating cylinder electrode study of the effect of activated polyacrylamide on surface roughness of electrodeposited copper, Hydrometallurgy **84**, 256-263 (2006).

[25] H.M.A. Soliman, H.H. Abdel-Rahman, The use of rotating cylinder electrode to study the effect of 1,3-dihydroxypropane on the production of copper powder, J. Braz. Chem. Soc. **17**, 705-714 (2006).

[26] I.Z. Selim, A.M. Ahmed, H. Soliman, Effect of ethylene glycol addition on copper electrodeposition using rotating cylinder electrode, J. Appl. Electrochem. **17**, 203-214 (2001).

[27] C. Du, Q. Tan, G. Yin, J. Zhang, 5 – Rotating Disk Electrode Method, in: W. Xing, G. Yin, J. Zhang (Eds.) Rotating Electrode Methods and Oxygen Reduction Electrocatalysts, Elsevier, Amsterdam, 2014, pp. 171-198.

[28] G. Denuault, M. Sosna, K.-J. Williams, 11 – Classical Experiments, in: C.G. Zoski (Ed.) Handbook of Electrochemistry, Elsevier, Amsterdam, pp. 431-469, 2007.

[29] F.C. Walsh, G. Kear, A.H. Nahlé, J.A. Wharton, L.F. Arenas, The rotating cylinder electrode for studies of corrosion engineering and protection of metals – An illustrated review, Corros. Sci. **123**, 1-20 (2017).

[30] O. Ige, R. Barker, X. Hu, L. Umoru, A. Neville, Assessing the influence of shear stress and particle impingement on inhibitor efficiency through the application of in-situ electrochemistry in a CO2-saturated environment, Wear. **304**, 49-59 (2013).

[31] E. Yariv, I. Frankel, The Diffusion-Control Limit Revisited, PRL. **89**, (2002).

[32] G. Orhan, G. Hapçı, Effect of electrolysis parameters on the morphologies of copper powder obtained in a rotating cylinder electrode cell, Powder Technol. **201**, 57-63 (2010).

[33] M.G. Pavlović, Š. Kindlová, I. Roušar, The initiation of dendritic growth of electrodeposited copper on a rotating disc electrode with changing copper concentration and diffusion layer thickness, Electrochim. Acta. **37**, 23-27 (1992).