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PRODUCTION OF COPPER POWDERS FROM WATER-DIMETHYLSULPHOXIDE ELECTROLYTES

Abstract. Electrodeposition copper powder of cathodic reduction in organic solvent is investigated and the electrolyte, representing solution $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in dimethylsulphoxide (DMSO) is offered. Varying concentration of electrolyte within the limits of 0,1-0,6 M and cathodic density of a current 200-1200 A/m^2 , at temperatures 288-348 K it is possible to receive qualitative copper powders with a given structure and dispersity. In work the electrolyte on the basis of aprotic polar solvent – dimethylsulphoxide was elaborated and the optimum conditions permitting to obtain electrolytic copper powders with high current efficiency, which differ in microstructure and morphology were determined. The structure electrolytic copper powders received electrolysis of 0,1-0,6 M of solutions $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO is studied depending on key parameters of a mode electrolysis - cathodic density of a current and temperature by the roentgenographical analysis.

Key words: Electrodeposition, dimethylsulphoxide, copper(II) nitrate crystalhydrate, current density, copper powder, roentgenography.

Introduction. Among developing directions of modern researches fine-dispersed powders have the particular interest. A microstructure of fine-dispersed powders gives them a number of new properties in comparison with usual materials. Recently it is given the great consideration to fine-dispersed copper powders possessing specific properties thanks to which it is possible their application for development of new effective materials of different purpose [1].

The basic application field of copper powder is powder metallurgy, where it is used for development of various products of constructional, antifriction and electrotechnical purposes, and also composite materials. In so doing copper powder is an intermediate product of copper manufacture and should meet the certain requirements. The electrolytic method allows producing chemically pure copper powders, which have unique, stable properties (a dendritic shape, a dense texture of particles). The basic advantage of the given method is a possibility of regulation of a powder's structure and properties by means of variation of electrolytic deposition parameters and an electrolyte composition. It allows to influence a structure, a size, a shape and a chemical composition of powders [2,3].

A problem of metals' isolation without the accompanying (parallel) reaction of hydrogen release, characteristic for electrolysis of water solutions, can be solved if to use the solvents possessing higher electrochemical stability, than water. Aprotic organic solvents, which do not contain mobile hydrogen and can be reduced at sufficiently high cathodic potentials, are the most admissible in this respect [4-6]. In this connection, in the given work as a solvent it has been chosen dimethylsulfoxide ($\text{CH}_3)_2\text{SO}$ – a cation-tropic compound describable by a high dissolving and ionising ability ($\epsilon=47$). Also it is known high adsorption activity of the solvent on a border «copper-electrolyte» [7].

In the work influence of various parameters has been investigated: a current density, temperatures and concentrations for the electroreduction of copper(II) ions in DMSO, a composition and purity of the copper powders produced.

Electrodeposition of a copper powder has been carried out on an electrolysis installation [8] with consecutive switching on an electrolytic cell and a copper coulombmeter. The electrolysis has been performed in a glass constant-temperature electrolytic cell in volume of 150 cm³. Electrodeposition of a copper powder was carried out in galvanostatic mode at a temperature-controlled glass cell equipped with a vinyl plastic cap with parallel fixed anodes, without forced stirring. As a cathode using a cylindrical steel rod that is placed in the center of the lid. The soluble anodes used as a plate made of electrolytically pure copper. The advantage of using soluble anodes is that electrolysis for quite a long time can be performed.

As a direct current source has been applied a universal power supply UIP-2 providing high stabilisation of rectified current. Electric circuit current has been measured by a multirange ampere-voltmeter AVO-5MI.

Quality of the electrolytic powders produced has been estimated visually and according to the microphotos made by means of a scanning electronic microscope J.SM-840 at increase in 2000 times.

The X-ray structural analysis of copper electrolytic powders has been performed on a diffractometer DRON-2,0 (monochromatic CuK_α-radiation). The counter speed is 2 deg/min.

Experimental

The researches of volume and transport properties of copper(II) nitrate crystalhydrate solutions in DMSO have shown, that the electroconductivity maximum is observed in the 0,4 M solution of copper(II) nitrate in DMSO at 288 K, which is displaced to 0,6 M at higher temperatures [9,10]. In this connection, for study of a possibility of a copper powder electrodeposition from dimethylsulfoxide the copper salt's concentration interval was in the limits of 0,1-0,6 M. The solutions with the copper salt concentration of 0,5 M and higher have high viscosity, which decreases the metal ions' mobility.

In the electrolyte used for obtaining a copper powder as a result of the components' interaction probably are formed copper(II) ions, nitrate ions, and also solvated [Cu(DMSO)₄(H₂O)₂]²⁺ complexes and inclusion complex ions – [(CH₃)₂SONO₃]⁻ [11], causing electroconductivity of the solution. The influence of DMSO on the copper powder electrocrystallization is obviously connected with its surface-active and complexing properties.

At the current density of 200-300 A/m² it is observed the copper powder de- position, but with lower current efficiency (63-64%). With increase of the current density to 500 A/m² the powder becomes fine-crystalline. The current efficiency of copper powder makes 75-86%. The further growth of current density to 1200 A/m² leads to small decrease in the current efficiency to 81%. The results of copper powder electrodeposition from 0,1 M of Cu(NO₃)₂·3H₂O solution in DMSO at T = 288 K are represented in table 1.

Table 1 – Results of the copper powder electrodeposition from 0,1 M Cu(NO₃)₂·3H₂O solution in DMSO at T = 288K

№	i _k , A/m ²	CE, %	The powder exterior view and quality
1	200	63,8	dark brown, large dendrites
2	300	64,2	dark brown, coarse-grained
3	400	75,1	dark brown with tints of red, coarse-grained
4	500	86,3	dark red, grained
5	600	86,8	pink, fine-dispersed
6	700	87,9	pink, fine-dispersed
7	800	88,5	pink, fine-dispersed
8	900	88,9	pink, fine-dispersed
9	1000	89,5	pink, fine-dispersed fraction
10	1100	86,2	pink, fine-dispersed fraction
11	1200	81,1	dark pink, fine-dispersed

At the electrolysis with the minimum current density of 100 A/m² and temperature of 298 K the dark brown powders with large dendrites are isolated. In the microphoto zoomed in 2000 times it is well visible the crystallites in the size from 45 to 90 microns ingrown into a grained surface. The yield of copper powder on the current is equal 79,1 % (tab.2, fig.1, a).

Table 2 – Results of the copper powder electrodeposition from 0,1 M Cu(NO₃)₂·3H₂O solution in DMSO at T = 298 K

№	i _k , A/m ²	CE, %	The powder's exterior view and surface morphology (x2000)
1	100	79,1	dark brown, the crystallites in the size of 45-90 micron on the grained surface
2	250	84,2	dark brown, the lengthened crystallites from 30 to 100 micron
3	500	96,8	brown with tints of red, decrease of the grains' average size
4	600	97,3	pink-red, the dendrite-form grains
5	750	97,9	pink, the grains are smaller than at i _k = 500 A/m ²
6	800	98,2	dark pink, fine-dispersed
7	900	97,5	dark pink, fine-dispersed
8	1000	97,1	dark pink, fine-dispersed

At the current density increase to 250 A/m² the dark brown sediments are formed. The electron microscope research has shown that the surface consists from lengthened crystalline grains in the size from 30 to 100 microns. The current yield has increased to 84,2%. The copper powder morphology is represented on fig.1, b.

The further increase in current density to 500-750 A/m² leads to the formation of average size grains (fig.1, c).

The copper powders obtained are thickness-uniform, have the dendrite morphology and very high purity. The copper grains have a dendrite form. The current yield of the copper powder practically does not vary and is within 96,8-98%.

With the current density increase above 800 A/m² the current yield slowly falls; in this case the light pink fine-dispersed copper powders are precipitated (fig.1, d).

The increase of current density to 1000 A/m² leads to the isolation of fine-dispersed powders and causes side processes leading to the formation of by-products, which lower the copper powders' quality and current yield. The electron microscope research has shown that the powder surface represents a uniform layer of small dendrites not exceeding 35 microns (fig.1, e).

The minor temperature increase (to 298 K) of 0,1 M copper nitrate trihydrate- DMSO electrolyte influences the electrolysis indicators: the metal yield considerably increases; the limit of cathodic current density, which provides obtaining a high-quality copper powder rises. Hence, the temperatures increase from T= 288 K to 298 K is favourable to isolation of high-quality copper powders from diluted copper nitrate - DMSO solutions. In these conditions at the current density above 1000 A/m² there is the reduction of copper powders' quality and current yield.

A roentgenogram of the copper powder produced from a 0,1 M Cu(NO₃)₂·3H₂O - DMSO solution at current density of 100 A/m² and temperature of 298 K has the strongly pronounced peaks with reflections distinctive for pure copper: 1,277; 1,81 and 2,08 A^o, the reflection of 1,81 A^o is the most intensive one. The observable peaks testify to high purity and a crystal structure of the copper powder. With the increase of current density to 500 and 750 A/m² the roentgenograms are similar the previous one, but it is noticeably observed the increase in intensity of reflections of 1,277 A^o and 2,08 A^o.

The results of X-ray phase analysis of the copper powders produced at constant current density of 800 A/m² and different temperatures have shown, that at temperature of 298 K an absolutely pure powder is precipitated. On the X-ray pattern (fig.2) can observe the peaks, characteristic for pure copper (1,277 A^o; 1,81 A^o and 2,08 A^o).

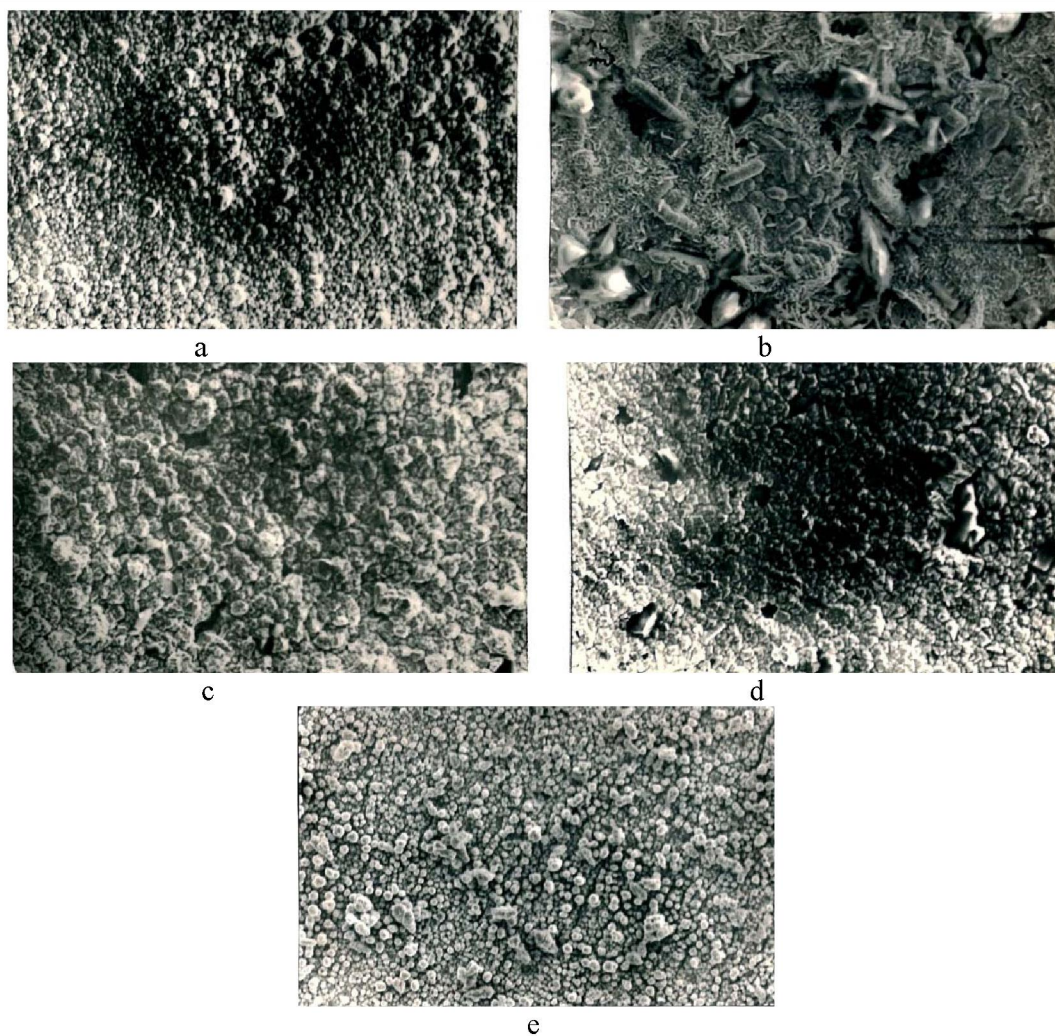


Figure 1 – Morphology of the copper powders produced from a 0,1 M solution of copper nitrate trihydrate in DMSO at temperature of 298 K and different current density: a – 100 A/m²; b – 250 A/m²; c – 600 A/m²; d – 800 A/m²; e – 1000 A/m² (zoom 2000)

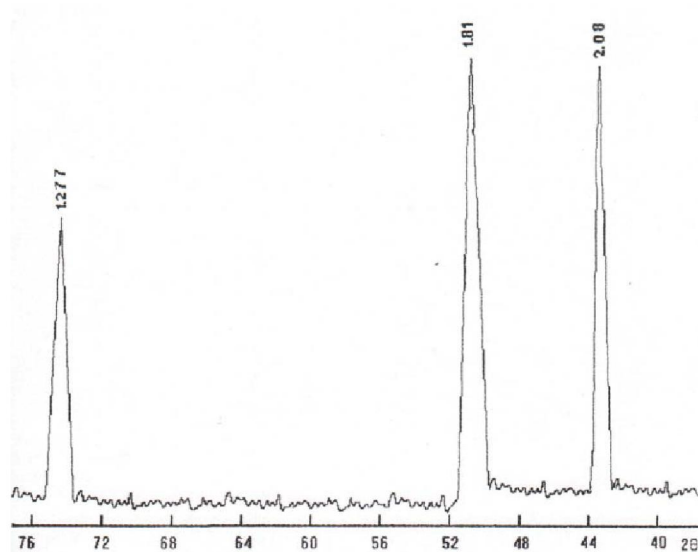


Figure 2 – An X-ray pattern of the powder produced from a 0,1 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ -DMSO solution at $i_k = 800 \text{ A/m}^2$ and $T = 298 \text{ K}$

Temperature effect on the copper electrodeposition from 0,1 M copper nitrate trihydrate - DMSO solution has been studied at current density of 800 A/m². The results are represented in table 3.

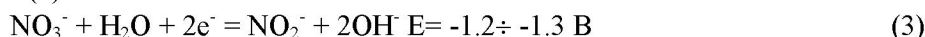
Table 3 – Results of the copper powder electrodeposition from a 0,1 M Cu(NO₃)₂·3H₂O-DMSO electrolyte at $i_k = 800 \text{ A/m}^2$ and different temperatures

№	T, K	CE, %	The powder exterior view and quality
1	288	88,5	pink, fine-dispersed
2	298	98,2	light pink, fine-dispersed, dense
3	308	94,5	light pink, separate strongly distorted crystal particles on medium-grained background
4	318	86,3	dark pink, grained, dispersed powder
5	328	84,0	dark pink, a surface of the powder is friable; small spheroidal crystallites
6	338	57,1	brick-red, coarse-dispersed
7	348	43,1	dark, coarse-dispersed

From the findings follows, that at the electrolysis of a diluted copper nitrate-DMSO solution the formation of high-quality powders is favoured by low temperatures to 298 K. In these conditions the basic cathode process happens on the equations (1) and (2).



With the rise of temperature to 308 K and above in the electrolyte occurs the breakage of hydrogen bonds that complicates the physicochemical processes and intensifies fluctuations in the solution. As a result of the breakage of nitrate ions-DMSO complexes the overstrain decreases and their reduction in accordance with the equation (3) is facilitated.



As a consequence, the nitrate ion reduction speed considerably increases pH of the cathode zone increases, the metal yield decreases and the powder quality sharply worsens. In the conditions of high basicity in the cathode area a probability of formation of copper(I) slightly soluble compounds, probably CuOH and Cu₂O, increases; these compounds, by-turn, are captured by the growing deposit and causes colouring the powder.

At the rise of temperature to 308 K the roentgenogram along with the pure copper reflections – 1,089 A°; 1,277 A°; 1,81 A°; 2,08 A°, contains reflections of other phase – 1,51 A°; 2,12 A° and 2,45 A°, which correspond to monovalent copper oxide Cu₂O; obviously, it forms owing to the interaction of copper(I) ions with hydroxyl ions and is joined to the cathode powder. Intensity of these peaks is insignificant.

At temperature of 318 K there are new peaks (1,283 A°; 3,00 A°) on the X-ray pattern (fig.3), which also are part of copper(I) oxide. The appearance of new peaks is obviously caused by the increase of copper(I) oxide amount in the copper powder. At the further increase in temperature (to 328 K) new peaks characteristic for copper(I) oxide are not observed, but intensity of the available peaks become stronger. Simultaneously intensity of the copper peaks 1,089 A° and 1,277 A° decreases (fig.4).

Inclusions of copper oxide Cu₂O formed on the cathode surface indicate the stepwise reduction of Cu²⁺ ions on the cathode.

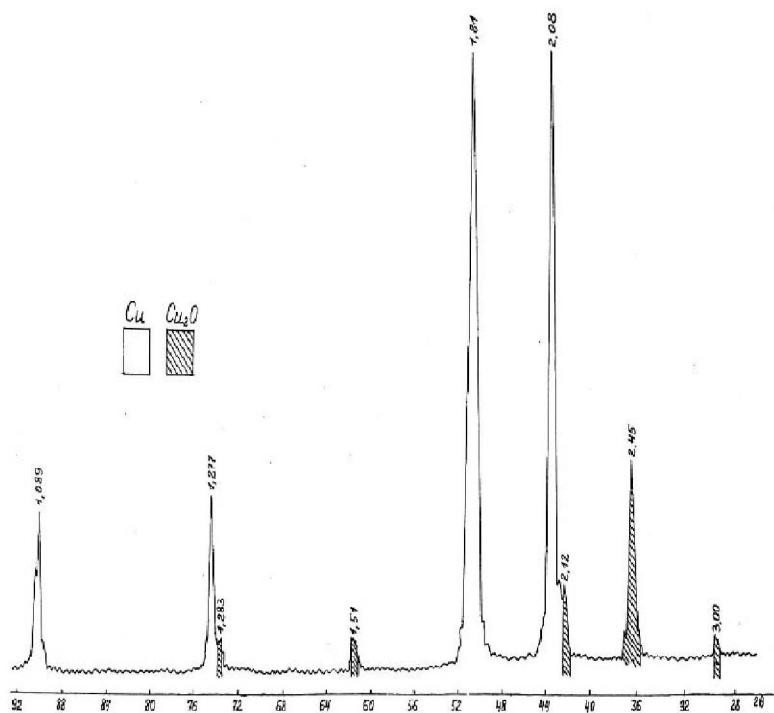


Figure 3 – An X-ray pattern of the powder produced from a 0,1 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ -DMSO solution at $i_k = 800 \text{ A/m}^2$ and $T = 318 \text{ K}$

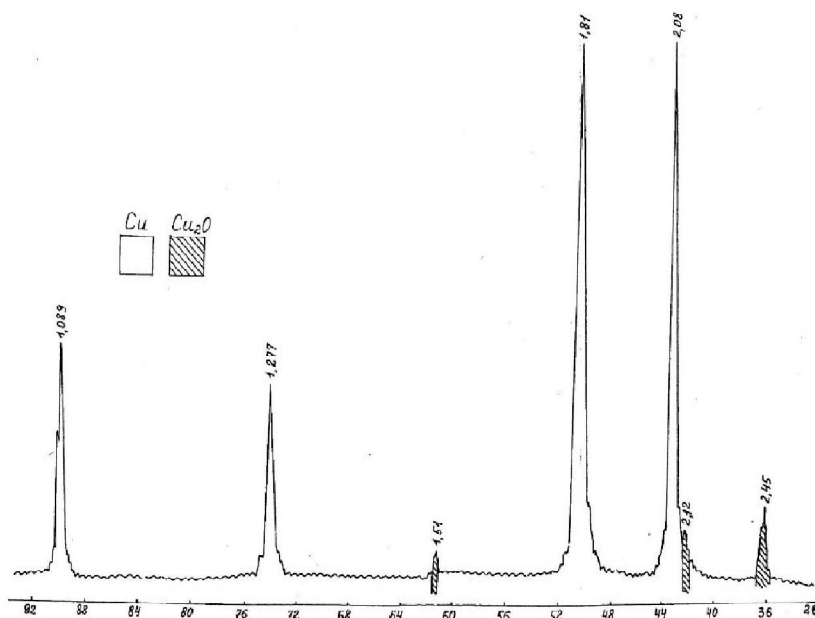


Figure 4 – An X-ray pattern of the powder produced from a 0,1 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ -DMSO solution at $i_k = 800 \text{ A/m}^2$ and $T = 328 \text{ K}$

The influence of various factors (concentration, temperature, current density) on the copper electrocrystallization from a dimethylsulfoxide electrolyte can be explained as follows.

The main cathode process is the reduction of copper ions expressed by the equations (1-2). Discharge of Cu^{2+} complex ions is connected with penetration through a dense adsorption film consisting of DMSO molecules.

It leads to the certain inhibition of complex copper(II) ion electroreduction. In these conditions, according to the theory, on the cathode it is isolated a more fine-dispersed copper powder, than at the electrolysis of water solutions of simple salts, which do not contain surface-active additives.

The rise of temperature (above 298 K) reduces adsorption activity of DMSO molecules, sharply increases reactionary activity of nitrate ions solvated by the molecules of an organic solvent in a less degree.

Presence of small water amounts in the solution (to 3,6 %), temperature growth and high polarization of the cathode most likely accelerate the reduction speed of more reactive nitrate ions; it leads to inclusion of copper(I) insoluble compounds in the cathodic powder, and, it is quite probable, the modification of growing metal crystals occurs at the expense of these compounds and not the solvent molecules.

The experiment results have shown that high-quality copper powders can be obtained from copper nitrate-dimethylsulfoxide solutions by means of electrolysis both diluted and concentrated solutions. From the diluted (0,1 M) solutions high-quality copper powders can be produced to 1000 A/m². Use of higher concentrations allows to produce qualitative coverings in wider interval of current density (in a 0,4 M solution – to 2200 A/m²).

The rise of temperature (above 303 K) and current density (above 1000 A/m²) causes the side reactions leading to formation of by-products; as a result of it the copper powder quality and yield decrease. The ion association, increasing with temperature growth, and increase of the electrolyte viscosity in concentrated copper nitrate trihydrate-DMSO solutions, reducing conductivity of the solution, cause difficulties of the copper ion reduction and quality loss of the copper powders produced.

The temperature effect on electrolysis in the investigated concentration interval has shown, that the rise of temperature to 303 K and above accelerates the reaction (2) reducing the copper current yield. In these conditions the accumulation of OH⁻ ions in the cathode zone, which is characterized by high basicity, leads to the formation of copper(I) oxide, which contaminates the cathodic deposit. The electrolytic deposits obtained are non-uniform by thickness, have an ordinary appearance. The presence of copper(I) oxide in the cathodic deposits is confirmed by the X-ray phase analysis data.

The temperature growth above 303 K also promotes the breakage of hydrogen bonds and disintegration of heteromolecular complexes on molecules of DMSO and H₂O. Also this phenomenon is probably accompanied by the dissociation of solvated complexes of copper(II) ions and inclusion complex ions, that creates the favorable conditions for electrolyte ion association; this phenomenon was confirmed by the results of transport properties of the solutions.

It is necessary to note the electrolytes, which contain 0,6 M of copper(II) nitrate crystalline hydrate. The copper yield from these solutions is lower than one from the diluted solutions. The copper powder obtained from such solutions has an unsatisfactory appearance in all interval of the investigated temperatures and current density. A dominant cause of it is the copper(I) sulphide formation and its inclusion in the powder. This supposition is confirmed by chemical and X-ray phase analyses.

Conclusion. Thus, the optimum conditions for obtaining high-quality fine-dispersed copper powders are concentration of 0,1-0,4 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and temperature of 283-298 K. The ion association, increasing with the temperature growth, and the increase of electrolyte viscosity in concentrated copper nitrate trihydrate-dimethyl sulfoxide solutions, reducing conductivity of the solution, cause the difficulties of copper ion reduction and deterioration of the powders produced.

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СУЛЫ-ДИМЕТИЛСУЛЬФОКСИДТІ ЭЛЕКТРОЛИТ ЕРІТІНДІЛЕРДЕН МЫС ҰНТАҚТАРЫН АЛУ

Аннотация. Жұмыста органикалық еріткіште мыс ұнтағын катодты тотықсыздану арқылы электротұндыруы зерттеліп, құрамында $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ және диметилсульфоксиді (ДМСО) бар ерітінді электролит ретінде ұсынылған. Электролиттің концентрациясын 0,1-0,6 М, катодты тоқ тығыздығын 200-1200 A/m^2 және температураны 288-348 К аралығында өзгере отырып, белгілі құрылымы мен дисперстілікке ие сапалы мыс ұнтақтарын алуға болады. Жұмыста апротонды полярлы еріткіш – диметилсульфоксид негізінде мыстың тұндыруына арналған электролит ұсынылған. Микроқұрылымы мен морфологиясы бойынша ерекшеленетін, тоқ бойынша жоғары шығымымен түзілетін мыстың электролиттік ұнтағын алудың оптималды жағдайлары анықталған. Электролиздің негізгі параметрлеріне – катодты тоқ тығыздығы мен температураға байланысты 0,1-0,6 М $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ – ДМСО ерітінділерден алынған мыстың электролиттік ұнтақтарының құрылымы рентгенографиялық талдаумен зерттелген.

Түйін сөздер: электротұндыру, диметилсульфоксид, мыс(II) нитратының кристаллогидраты, тоқ тығыздығы, мыс ұнтағы, рентгенография.

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ПОЛУЧЕНИЕ МЕДНЫХ ПОРОШКОВ ИЗ ВОДНО-ДИМЕТИЛСУЛЬФОКСИДНЫХ РАСТВОРОВ ЭЛЕКТРОЛИТОВ

Аннотация. Исследовано электроосаждение медного порошка путем катодного восстановления в органическом растворителе и предложен электролит, представляющий раствор $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ в диметилсульфоксиде (ДМСО). Варьируя концентрацию электролита в пределах 0.1-0.6 М и катодную плотность тока 200-1200 A/m^2 , при температурах 288-348 К можно получить качественные медные порошки с заданной структурой и дисперсностью. В работе предложен электролит на основе апротонного полярного растворителя – диметилсульфоксида и определены оптимальные условия, позволяющие получать электролитические порошки меди с высоким выходом по току, различающиеся микроструктурой и морфологией. Структура электролитических порошков меди, полученных электролизом 0.1-0.6 М растворов $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ в ДМСО изучена в зависимости от основных параметров режима электролиза – катодной плотности тока и температуры рентгенографическим анализом.

Ключевые слова: электроосаждение, диметилсульфоксид, кристаллогидрат нитрата меди(II), плотность тока, медный порошок, рентгенография.