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Электрокристаллизация медных порошков
из диметилсульфоксидных растворов**

**Mamyrbekova Aigul, Mamitova A.D.,
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Electrocrystallization of copper powders
from dimethylsulphoxide solutions**

Показана возможность электроосаждения медного порошка путем катодного восстановления из раствора электролита, содержащего тригидрат нитрата меди(II) и диметилсульфоксид (ДМСО). Исследовано влияние режимов электролиза: плотности тока, концентрации и температуры электролита на размерные характеристики полученных порошков меди. Размер и форму частиц полученных порошков определяли с помощью электронной микроскопии

Ключевые слова: диметилсульфоксид, тригидрат нитрата меди(II), электропроводность, медный порошок

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In this article the possibility of electrodeposition of copper powder by cathode reduction from a solution of the electrolyte containing copper(II) nitrate trihydrate and dimethylsulphoxide (DMSO) is shown. Influence of electrolysis regimes such as intensity of current, concentration and temperature of electrolyte on dimensional characteristics of the produced copper powder is investigated. The size and the form of particles of the received powder are determined by electronic microscopy

Key words: dimethylsulphoxide, copper(II) nitrate trihydrate, electrical conductivity, copper powder

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Today an actual problem is working out of new electrochemical methods of synthesis of finely divided copper powder. Process of reduction of metal on the cathode without accompanying reaction of hydrogen releasing, characteristic for electrolysis of water solutions, can be solved if to use the solvents possessing higher electrochemical stability, than water. Most suitable in this case are aprotic organic solvents which do not contain some mobile hydrogen and are reduced at rather high cathodic potentials [1, p. 134]. In this connection, in the given work as solvent it was chosen dimethylsulphoxide (CH₃)₂SO – the cation tropic connection characterised by high dissolving and ionising ability ($\epsilon=47$). It is known about the high absorption activity of solvent on the interface copper-electrolyte [2, p. 1165].

The electrolyte offered in the given work received by dissolution of trihydrate of copper nitrate Cu(NO₃)₂·3H₂O in DMSO, differs by simplicity of structure and thanks to presence of surface-active and complexing properties of ions Cu²⁺ and NO₃⁻ with solvent, does not require introduction of other additives influencing on kinetics of reduction of copper.

In this context, the purpose of the present work is production of finely dispersed powder of copper from water solutions of dimethylsulphoxide with the sizes of particles till 50 microns and studying of their physical and chemical properties.

Electrocrystallization of copper powder were spent in solutions of copper(II) nitrate trihydrate in DMSO. Used in work trihydrate was synthesized by a technique [3, p. 356] and was purified by recrystallization from a water solution. Chemical pure DMSO was exposed to vacuum distillation ($n_D^{25} = 1.4816$). The prepared solutions of electrolytes before electrolysis were held not less than a day for achievement in system of ionic balance.

Electrodeposition of copper powder was spent in galvanostatic regime in temperature-controlled glass box equipped by vinylplast cover with parallel fixed anodes, without forced mixing. A steel cylindrical core, placed in the cover centre, was used as the cathode. The plates made from electrical pure copper were used as the soluble anodes. The advantage of application of soluble anodes is the possibility of electrolysis carrying out for enough a long time.

After the termination of electrolysis the received precipitate was repeatedly washed out by bidistilled water till constant value of conductivity of washing water and dried up till powder with constant weight.

The size and the form of particles of the received powder were determined by electronic microscopy. In work raster electronic microscope JSM 6490 LA was used that increases in 2000 times.

For studying of the distribution by the sizes of copper powder particles the laser analyzer of mark LS 13 320 with the water module was used. The range of measurement of the size of particles fluctuates from 0.020 microns to 200 microns. For measuring of particles by diffraction method the laser light with the length of a wave of 750 nanometers, generated in the ultrasonic radiator of the device LS 13 320, was used.

X-ray structural analysis of electrolytic powder copper is executed on diffractometer DRON-2.0 (monochromatic CuK_α - emission). Speed of rotation of the counter is 2 deg/min.

Polarization measurements were spent in potentiodynamic regime with use of potentiostat PI-50-1. Speed of development of potential is 5 mV/second. The platinum wire was used as working electrode on which in standard conditions by electrolytic way a layer of copper with the thickness of 18-20 microns was electroplated. As a comparison electrode the silver electrode $\text{Ag}/0.01 \text{ M AgNO}_3$ in DMSO [4, p. 298] was used which potential is measured in relation to saturated mercurial sulphatic electrode $\text{Hg}/\text{Hg}_2\text{SO}_4$, 1 n H_2SO_4 and in recalculation on a hydrogen scale it was +0.3 V.

The researches of volume and transport properties of solutions of copper(II) nitrate trihydrate in DMSO have shown that the maximum of conductivity is observed in 0.4 M solution of copper(II) nitrate in DMSO at 15°C that is changed till 0.6 M at higher temperatures [5, p. 415]. In this connection, for studying of possibility of electrodeposition of copper powder from dimethylsulphoxide the interval of concentration of copper salt was chosen 0.1-0.6 M. In solutions with concentration of 0.5 M of copper salt in DMSO and higher the viscosity is considerably raised that reduces the mobility of ions of metal.

In electrolyte for producing of copper powder, as a result of interaction of components the ions of copper(II), nitrates-ions, and also solvated complexes $[\text{Cu}(\text{DMSO})_4(\text{H}_2\text{O})_2]^{2+}$ and ion-adducts $[(\text{CH}_3)_2\text{SONO}_3]^-$ are possibly formed, causing electroconductivity of solution. Influence of dimethylsulphoxide on electrocrystallization of copper powder is connected, obviously, with its surface-active and chelating properties.

Laws of kinetics of cathodic processes of electrochemical deposition of copper from dimethylsulphoxide solutions of copper nitrate trihydrate was studied in potentiodynamic regime in 0.4 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO at temperatures 25-55°C.

At temperature of 25°C the cathodic voltage-ampere curves are the curves with two accurately expressed maximums of currents that proves the two-step discharge of solvated complexes of copper(II) $[\text{Cu}(\text{DMSO})_4(\text{H}_2\text{O})_2]^{2+}$ on electrode adsorbed by molecules of dimethylsulphoxide that schematically can be presented as:

Formation of dimethylsulphoxide complexes of copper(II) and formation of enough dense adsorbed layer on the cathode, consisting of molecules of organic solvent lead to certain braking and shift of potential of restoration of copper(II) ions in more electronegative area ($E = -0.5 \text{ B}$) and promotes formation of finely divided copper powder.

At temperatures 35-55°C the third wave which lies in deeper area of electronegative potentials is observed on polarising curves. Probably this maximum corresponds to restoration of nitrates-ions:

Rise of temperature till 35°C and higher, obviously, promotes partial desorption of solvent, hydrogen bond opening between molecules of H_2O and $(\text{H}_3\text{C})_2\text{SO}$, causing destruction of heteronuclear complexes, also the fluctuations of structure connected

with disintegration of nitrate complexes strengthen. Hence, these processes promote to acceleration of process of nitrates-ions restoration, less solvated by molecules of organic solvent, that causes their great reactivity with temperature growth.

With increase of concentration of copper(II) salt in organic solvent the offset of cathodic potential to more electronegative meanings is observed that leads to decrease of maximums and sizes of cathodic currents. The given phenomenon is possible to explain by increase of viscosity of solution, decrease of dissociation degree of copper(II) nitrate trihydrate in DMSO, and also reduction of copper ions diffusion coefficient.

In solutions of higher concentrations (>0.6 M) the ionic association is strengthened that cause the viscosity increase, reduction of dielectric permeability and decrease of electro conductivity, established earlier.

The size and the form of particles of the received powder were determined by the microphotos, received by raster electronic microscope JSM 6490 LA. For each preparation of copper powder, received after electrolysis, some microphotos were made that provided possibility of determination of disperse structure of powder.

The chemical compound of the received copper powder is determined by X-ray phase analysis.

From the received data it follows that at electrolysis of the diluted solution of copper nitrate in DMSO the low temperatures till 25°C promote formation of qualitative powder. In these conditions on the cathode the basic process according to the equations (1) and (2) proceeds. With rise of temperature till 35°C and higher the hydrogen bonds are broken in electrolyte that causes complication of physical and chemical phenomena and to strengthening of fluctuations in solution. As a result of destruction of complexes of nitrates-ions with DMSO, the overpressure decreases and their restoration according to the equation (3) is lightened.

As a result the speed of restoration of nitrate-ions and pH of cathode zone increase, the yield of metal decreases and powder quality sharply worsens. In the conditions of the raising of alkalinity in the cathode area the probability of formation of slightly soluble compounds of copper(I), probably CuOH and Cu_2O , increases which are captured by a growing precipitate causing certain colouring of the powder.

Formed inclusion of copper oxide Cu_2O on the surface of the cathode which are proved by X-ray pictures, tell about step restoration of Cu^{2+} ions on the cathode.

Thus, by a method of electrochemical synthesis the fine disperse copper powder with the sizes of particles till 50 microns from dimethylsulphoxide water solutions are received and their physical and chemical properties are studied. It is established that the powder produced from 0.1-0.4M solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO has the maximum content of particles with the sizes of 30-40 microns. By the results of a radiographic method of research it is determined that the structure of the received powder contain Cu and Cu_2O .

Список используемых источников:

1. Nomberg M.I. *Production of a copper powder by electrolytic way*. M: Metallurgy. 1971. P.134.
2. Vahidov R.S. *Electrodeposition of copper from nonwater solutions*//*Electrochemistry*. 1994. V.30. N 97. P. 1165-1166.

3. Karyakin U.V., Angelov I.I. *Pure chemical substances*. M: Chemistry. 1974. 408 p.
4. Kudryavtseva V.N., Varypaev V.N. *Practical work on applied electrochemistry*. L: Chemistry. 1990. 304 p.
5. Mamyrbekova A.K. *Concentration Dependences of the Density, Viscosity, and Refraction Index of Cu(NO₃)₂·3H₂O solutions in DMSO at 298 K*//Russ. J. Phys. Chem. 2013. V.87. N3. P.414-417.

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