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ARTICLE

Physico-chemical Properties of Fine Powders of Copper Obtained by Electrochemical Synthesis

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ABSTRACT

The possibility of electroprecipitation of copper powder *via* cathodic reduction of an electrolyte solution containing copper(II) nitrate and dimethyl sulfoxide is reported. The physico-chemical analysis of fine powder of copper received from water containing dimethyl sulfoxide solutions is conducted. Particle sizes of the copper powder are defined by a submicroscopy. The qualitative composition of copper powder is determined by results of radiographic and thermogravimetric techniques. By results of physico-chemical properties of fine copper powders prepared by an electrochemical cathodic deposition it is established that the anode material practically does not influence, their chemical composition and dimensional characteristics.

KEYWORDS

Dimethyl sulfoxide, Copper powder, Electrolysis, Thermogravimetry.

INTRODUCTION

The microstructure of fine powder gives a number of new properties in comparison with usual materials. Recently, a study represents applications of fine copper powder for creation of new effective materials of different function [1]. Determination of dependence of structure and properties of produced the copper powder from structure of electrolyte is actual problems of electrochemistry. It is necessary to notice that the application of a copper powder in mechanical engineering essentially reduces a friction, capacity of engines thereby raises and increases their toughness. The copper powder can be used by manufacture of electronic schemes, fly-wires, electrodes, electro- and heat conducting pastes. Copper powder improve sintering processes in powder metallurgy [2]. With development of electronic techniques and electronic equipment and tendency to miniaturization of devices, the replacement of precious metals on materials, based on nano-powder of copper which is much cheaper and more accessible as they do not concede on electroconductivity the precious metals and plasticity.

Production of high active fine copper powder, the offered electrochemical method, in comparison with others, is preferable because of low-cost price and form of powder particles surface. The given electrochemical method of a copper powder synthesis, finding wide application in chemical, metallurgical

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and other industries, is one of competitive ways as it is based on use of stationary modes of electrolysis and also has following advantages *viz*., simplicity of the equipments necessary for synthesis which is spent at atmospheric pressure and normal temperature, at insignificant power expenses. The copper powder produced by electrolysis, possesses morphology of dendrites and high degree of chemical cleanliness. Varying concentrations of electrolyte, cathodic density of a current, temperature it is possible to receive electrolytic deposits of copper differing by microstructure and morphology [3].

The production of copper powder with the set properties package gives the possibilities for creation of new effective catalysts with the great specific surface, electroconductive materials, effective lubricants, alloys, composite materials of different function, and also preparations with high biological activity for application in medicine and agriculture. A review about copper electrodeposition from non-aqueous solutions it is necessary to notice, that the references contain the information about a possibility of copper deposition from DMSO-based solutions or using DMSO as an additive. Copper (I, II) sulphate, acetate, chloride and copper(II) bromide are used as electrolytes. The analysis of available literary data has shown that systematic researches on copper electrodeposition from DMSO have not been carried out. The study of physico-chemical or electro-chemical properties of other copper compounds, in particular copper nitrates, in DMSO or DMSO-H_2O mixtures in references not found.

In this connection, study of physico-chemical properties of trihydrate of copper nitrate solutions in DMSO, conditions and laws of cathodic reduction of copper from these solutions with the purpose of a fine-dispersed copper powder production are timely.

EXPERIMENTAL

Electrocrystallization of copper powder was done in solutions of copper(II) nitrate trihydrate in DMSO according to the reported technique [4] and purified by recrystallization from a water solution. 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 of ionic balance. Electrolyte for receiving a copper powder from non-aqueous solution (DMSO) as the donor of ions of copper contains copper(II) nitrate at the following ratio of components:copper(II) nitrate = 0.1-0.4 mol/l; DMSO - upto 11.

Electrodeposition of copper powder was spent in galvanostatic regime in temperature controlled glass box equipped by viniplast 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 a longer time. Termination criteria of electrolysis process was active during the release of hydrogen. After the termination of electrolysis, the obtained precipitate was repeatedly washed out by double distilled water and dried up till powder with constant weight is obtained.

The size and the form of particles of the received powder were determined by electronic microscopy. In this work, Raster electronic microscope JSM 6490 LA was used that increases in 2000 and 5000 times. For study 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 to 200 μ. For measurement of particles by diffraction method the laser light with the wavelength of 750 nm, generated in the ultrasonic radiator 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 conducted in potentiodynamic regime using potentiostat PI-50-1. Speed of development of potential is 5 mV/s. The platinum wire was used as working electrode on which in standard conditions by electrolytic way a layer of copper having thickness of 18-20 μ was electroplated. As a comparison electrode the silver electrode Ag/0.01 M $AgNO_3$ in DMSO [5] was used for which potential is measured in relation to saturated mercurial sulphatic electrode Hg/Hg_2SO_4, 1 N H_2SO_4 and in recalculation on hydrogen scale was + 0.3 V.

Thermogravimetric analysis of cupriferous powders were conducted on Micro-thermo weights TG 209 F1 at the temperature range from 20 to 960 ºC at rate of heating 10 K/min. Heating of powders was performed in air and argon atmospheres. Calorimetric measurements were taken on the differential scanning calorimeter of 204 F1 brand of NETZSCH in the range of temperatures from 20 to 600 ºC in air and argon atmospheres. Powder with the greatest number of particles less than 100 nm in size was investigated by methods of an electron diffraction investigation, roentgenography and thermogravimetric.

RESULTS AND DISCUSSION

The results of volume and transport properties of solutions of copper(II) nitrate trihydrate in DMSO have shown the maximum conductivity observed in 0.4 M solution of copper(II) nitrate in DMSO at 15 ºC is changed till 0.6 M at high temperatures [6]. In this reference, for studying the possibility of electro-sedimentation of copper powder from DMSO, various concentrations of copper salt were chosen from 0.1 to 0.6 M. In solutions with concentration of 0.5 M of copper salt in DMSO and higher the viscosity is considerably raised which reduces the mobility of ions of metal.

In electrolyte for producing the copper powder, as a result of interaction of components the copper(II) ions, nitrates ions, and solvated complexes $[Cu(DMSO)_4(H_2O)_2]^{2+}$ and ion-adducts $[(CH_3)_2SONO_3]^-$ are possibly formed [7], causing electro-conductivity of solution. Influence of DMSO on electrocrystallization of copper powder is due to the surface-active and chelating properties.

The results show that the variation of chemical composition of electrolyte allows to influence structure, a size, form and chemical composition of powders. In particular, variation of parameters of an electrolysis gives the chance to influence parameters of a form of particles, a specific surface area, size of a copper powder and also processing behaviour of powder (bulk weight, compactibility, *etc*.). Variation of parameters of an electrodeposition, namely current density, temperature of

electrolyte, cathode form (plate and core), gives the chance to influence parameters of a form of particles, such as specific surface area and also size of deposited cathode. Variation of concentration of DMSO electrolyte also allows to influence structure, a size, a form and chemical composition of powders, allows to receive powders of more high quality with the increased processing behaviour. Time change should not decrease current efficiency as one of the key economic indicators of process of an electrolysis creates difficulties.

The size of obtained coppers powders at 25°C, concentration of electrolyte of 0.4 M and various density is defined from electronic and microscopic pictures. High resolution power of a microscope allowed to determine the size of shallow parts which was ranging from 10 to 120 nm. Electronic and microscopic images (Figs. 1 and 2) of powder represent the distribution sizes of electrochemical restored cupriferous particles. Apparently from micrographs, the structure of a dispersible deposit represents an assembly of particles with sizes from 20 to 120 nm. Large particles represented a loosely coupled units and spherical can take the form of more shallow particles with sufficient degree of nearness.

From the thermogravimetric analysis curves of change of mass of copper powder air atmosphere, it is possible to allocate two sites for the obtained powder with use of both soluble and insoluble anodes. The first curve is in an interval of temperatures upto 200 ºC which shows slight decrease of mass of copper powder, bound to solvent evaporation. The second curve at temperatures above 200°C corresponds to increase in mass of copper powder owing to oxidation of components of powder (Figs. 3 and 4).

The thermogravimetric analysis of mass of copper powder when heated in argon atmosphere using a soluble anode in all temperature range (from 20 to 940 ºC) decrease of mass of copper powder and the gradual evaporation of solvent was also observed. Results of DSC of copper powder using soluble anode showed that it is also possible to allocate two intervals for curve DSC (Fig. 5). In temperature range from 20 to 220 ºC, on curve the minimum corresponding to thermonegative process (solvent evaporation) is noted. Further increase in temperature up to 600°C, the excess and a maximum corresponding to intensive exothermic processes, which results to oxidation of components of powder, were observed. At temperature about 400 ºC, there is an oxidation of copper to CuO on the following equation of reaction:

$$2Cu + O_2 = 2CuO \quad (1)$$

Further heating results to the oxidation of Cu_2O to CuO and oxidation of copper to Cu_2O as per according to the following equation:

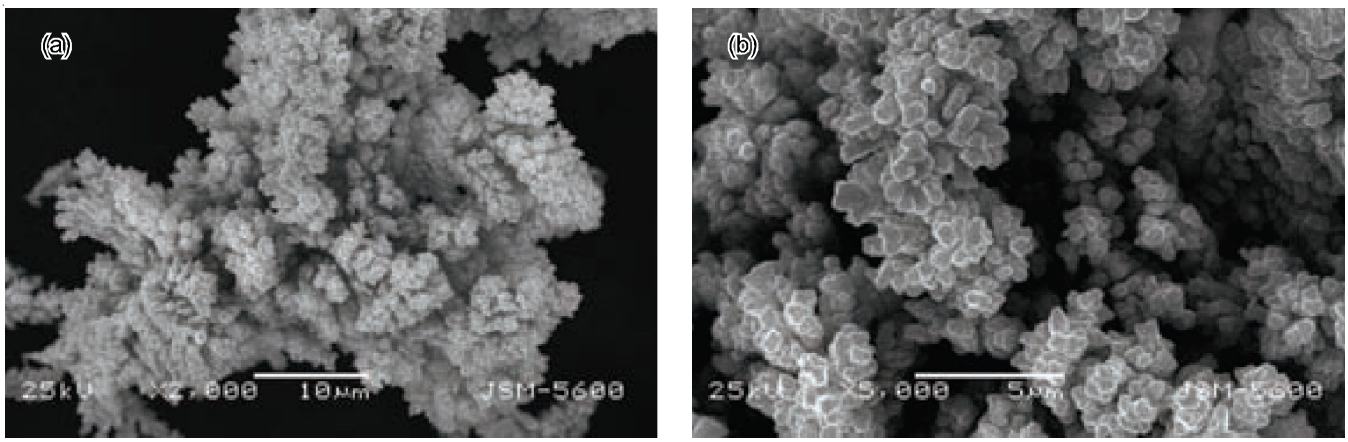

Fig. 1. Morphology of the copper powders received from 0.4 M solution of copper nitrate trihydrate in DMSO at current density 900 A/m^2 (a-x2000, b x5000)

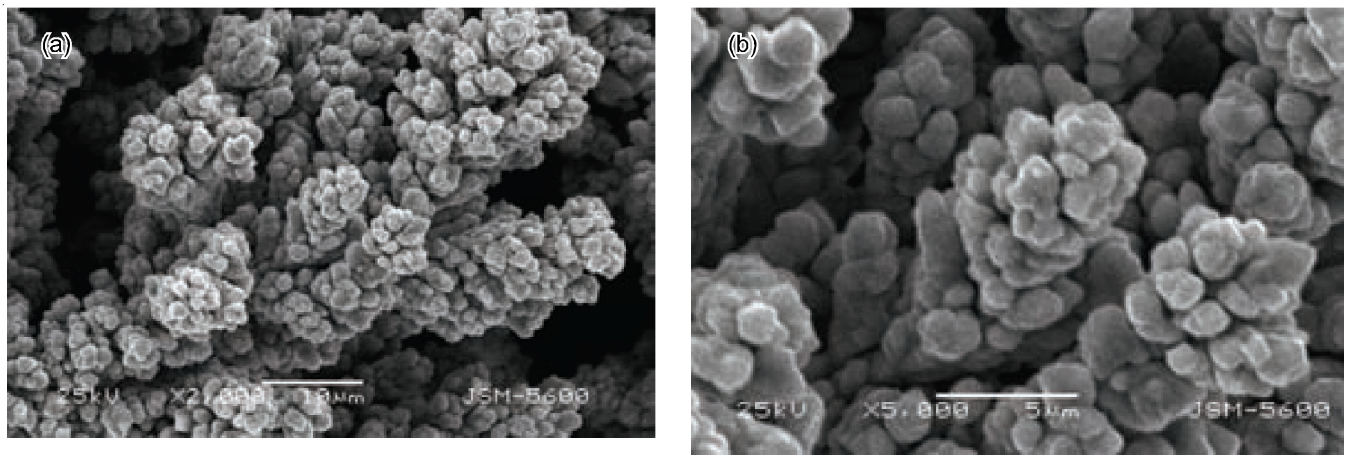

Fig. 2. Morphology of the copper powders received from 0,4 M solution of copper nitrate trihydrate in DMSO at current density 1000 A/m^2 (a x2000, b x5000)

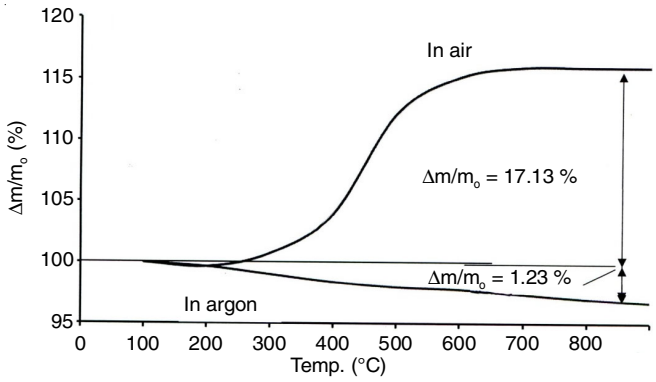

Fig. 3. Thermogram of the powder received with use of a soluble anode

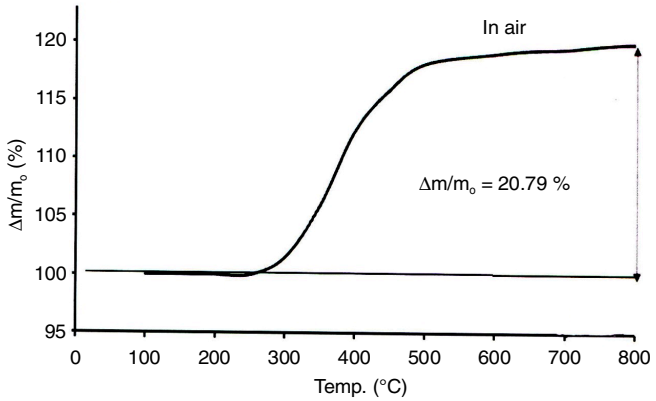

Fig. 4. Thermogram of the powder received with use of the insoluble anode

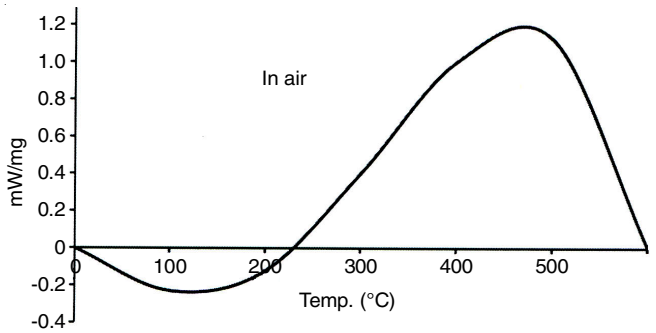

Fig. 5. Differential scanning calorimetric of the powder received with use of a soluble anode

$$2Cu_2O + O_2 = 4CuO \quad (2)$$

$$4Cu + O_2 = 2Cu_2O \quad (3)$$

Upon termination of thermogravimetric experiments in a crucible there is a powder of black colour which corresponds to CuO. By results of the conducted experiments of physico-chemical properties of the fine powders of copper received by an electrochemical cathodic deposition, it is established that the anode material practically does not influence their chemical composition and dimensional characteristics.

Conclusion

The crucial role in formation of finely divided particles is played by concentration of electrolyte. Technical plan and perspective for carrying out an electrolysis with soluble (copper) anodes is more economic. Optimum concentration of electrolyte for electrochemical synthesis of ultra-dispersible powders is 0.4 M.

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