УДК 544.65

Є.В. Павленко, магістрант
С.Г. Єгоров, доцент, к.т.н.

MODERN METHODS OF RECEIPT OF COPPER POWDER WHICH CONTAINS NANOFACTIONS

Zaporozhe state engineering academy, Ukraine

The analysis of spraying method, physical-chemical and electrolytic methods for a copper powder production has been carried out. The technological schemes of mentioned methods have been offered and its short description was given. It is determined that for the production of the copper powder containing nanofraction, the electrolytic method is the most admissible, iallowing to control by properties and by quantitative exit nanofraction. Additions to a sulphate electrolyte of gelatin and polyethyleneglycol raisesa increase an exit nanofraction properly in 6 and 10 times.

Key words: spraying method, method of autoclave treatment, cementation, an electrolysis, a copper powder, nanofactions, surfactants

Entry. For creation of new multifunction materials in the last time apply copper nanopowders [1,2]. His use improves the process of sintering in powder-like metallurgy, promotes quality of powder-like steels, provides conductivity and high mechanical properties of polymers and others like that. Introduction of the noted nanopowders to plastic lubricating materials promotes them anti-friction and tribological descriptions. Due to ability to retain high and proof conductivity copper nanopowders use in electronics, and also as catalysts in chemical industry [3].

For the production of nanopowders of copper as a rule apply an electrolytic method, however there are other methods: method of electric explosion of explorer, technology of evaporation-condensation, sol-method, chemical renewal and others like that. An electrolytic method is more valuable method, however allows to get clean powders of copper, which are unique, stable characteristics (dendrite form, dense texture of particles), chemically. Also this method provides adjusting of properties of powder by varying of parameters of electrode position and composition of electrolyte [4,5]. Introduction in the complement of electrolyte of chemically-active connections allows to get more stable powders with the increased technological properties and necessary size of particles [6,7]. The lack of copper powders, got an electrolytic method, is relatively a largeness of parts of powder (50...200 мкм), while modern industrial technologies need the use of micro powders (by the size of to 10 мкм) and nanopowders.

Raising of task. To compare the existent methods of production of copper powder to the purpose of determination of the most corresponding method of receipt of copper powder which contains nanofactions, and also to define the technological parameters of process, which most influence on the output of nanofactions and morphology of particles of powder.

Main part of researches. For the production of copper powders, as a rule, use the method of dispersion, and also physical and chemical and electrolytic methods.

The method of dispersion consists in crushing of stream of fusion gas or water. Get powders of high-purity and homogeneous composition such method with the

set of particles after sizes and necessary form. The flowsheet of the noted method is given on rice.1.

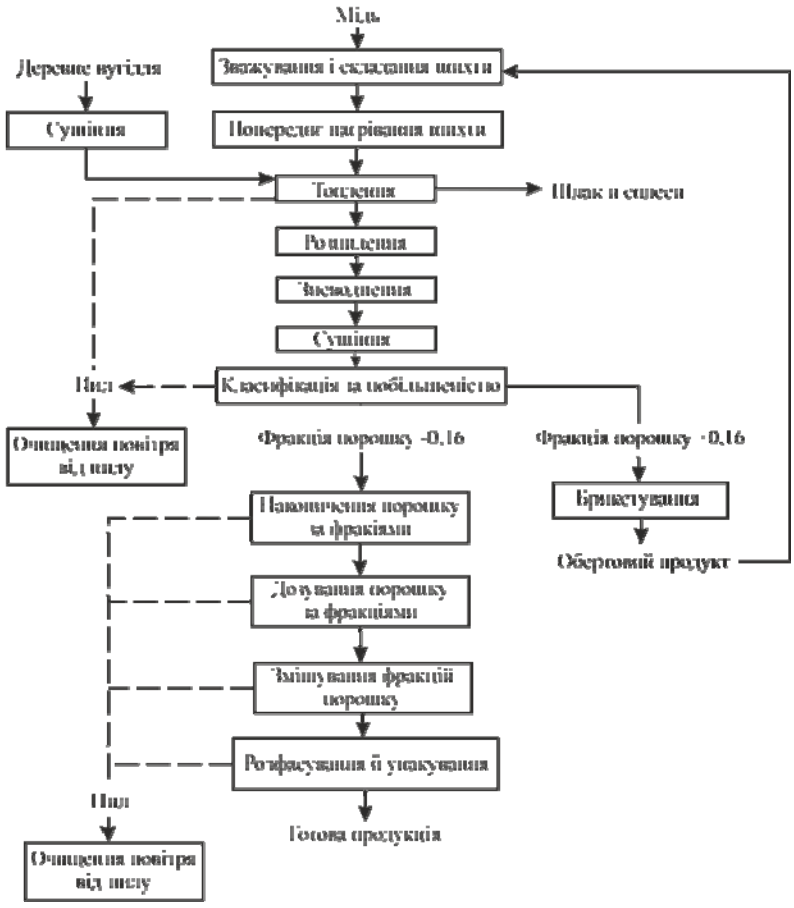

Figure 1. Chart of production of copper powders by dispersion of fusion by water of high-pressure [3]

On the area of preparation of charge the letters of cathode copper (brands of M0, M1) cut scissors to pieces, which are comfortable for loading in a stove. Components of charge weigh on scales, warm up to the temperature 420 K for moving away of moisture and conclude in baskets which give to the melting separation. Melting is executed in induction stoves, which, at a necessity, apply as mixers for overburning and leading to of fusions, prepared in other stoves. Fusion of copper (on 270 degrees higher than temperature of melting) is warmed-up unite to the hearth, preliminary warmed-up to the temperature 1100...1150 K, where his surface is covered by a charcoal. From a hearth fusion acts a stream to the area of nebulized, where him dispergate the streams of water of high-pressure. The created mash of powders of copper is given to the vacuumized filters of batch-type, where get powder with humidity to 5 %, which is farther added to drying in a convective pipe-dryer by the ascending stream of the heated gases.

Comfortably to get powders of fusible metals and alloys the method of nebulized with the temperature of melting below 1800 K. Nebulized is especially effective at the production of powders of multicomponent alloys (bronze and composition-metal). A form of particles of powders is spherical or triplepane. To the lacks of

method it follows to take the necessity of work with fusions at a high temperature and high pressure which needs presence of the special equipment and high qualification of operators. Besides, powders which get this method, 2,0...4,5 gs/cm^3 have a bulk closeness, at that time as electrolytic powders of copper have a bulk closeness 1,25...2,70 gs/cm^3, that allows to get more high-quality details from these powders.

The physical and chemical methods of receipt of copper powder are related to treason of chemical composition of raw material as a result of deep physical and chemical transformations: cementation (chemical dissolution is with further renewal) and autoclave method.

During cementation copper powder is besieged from solution by basers - zinc dust (with the size of particles a 0,1...0,4 mm) the expense of which is determined taking into account remaining content of copper in solution for stoichiometry reactions $Cu^{2+} + Zn = Zn^{2+} + Cu$. Sulfate solution contains 50 kg/m^3 copper and 5...20 kg/m^3 of sulphuric acid which hinders to the hydrolysis of admixtures. An additional factor which provides the cleanness of copper powder (97,0...98,5 % Cu) is high remaining maintenance of copper in solution (1...2 kg/m^3). A process is carried out for temperatures 323 K in agitators with mechanical mixers; eventual mash is filtered, powder is washed by water, stabilize a 0,05 % solution of soap and add to drying [3].

In an autoclave method a copper it is proceeded in by hydrogen from solutions of her salts at the increased temperature and pressure. Chart of production of copper powder from secondary raw material, cementine copper and copper concentrates, mattes, solutions which act from a contiguous production, it is given an autoclave method on rice. 2. Most there is a chart of processing of metal-backer secondary raw material and different cakes of cementine copper an outage.

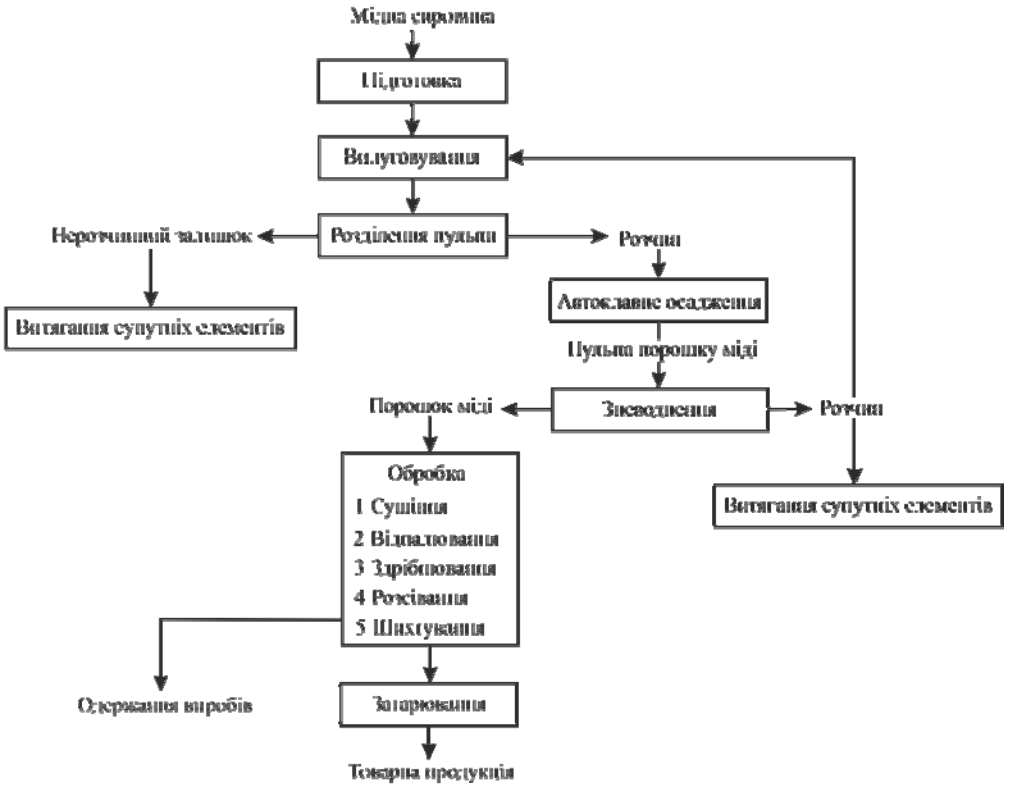

Figure 2. Chart of autoclave method of receipt of copper powder [3]

The use of sulfide raw material diffuses the source of raw materials of production of copper powder substantially, however it becomes complicated by the bulky chart of lixiviating and treatment of mash, and also problem of exception of noble metals. Advantages of chart are the use of various cheap raw material, insignificant running expenses, profitability of production even at small scales.

An electrolytic method consists in the electrolysis of aquatic sulfate solutions of copper with soluble anodes at certain terms. The fundamental chart of receipt of copper powder is brought such method around to rice. 3.

An electrolysis is executed in baths of bunker type with the bottom unloading of copper powder, where anodes (copper of brand of M-0) are poured, and cathodes - cored. Electrolyte from pressure tanks enters a drift electrolysis baths; after passing through baths of him collect in receiving tanks, and then pump over through heat exchangers, where carry out heating to the temperature 368 K in pressure tanks. Speed of circulation presents 45...60 l/min on one bath.

For maintenance of constancy of composition of electrolyte his part is destroyed on a regeneration. Adjustments of composition of electrolyte execute constantly a scourage and sulphuric acid. Unloading of powder carry out one time on five twenty-four hours. Anodic bits and pieces wash and order to the meltback and casting of anodes. Powder as mash with correlation of T : P = 1: 7 acts on the stage of the wet defending.

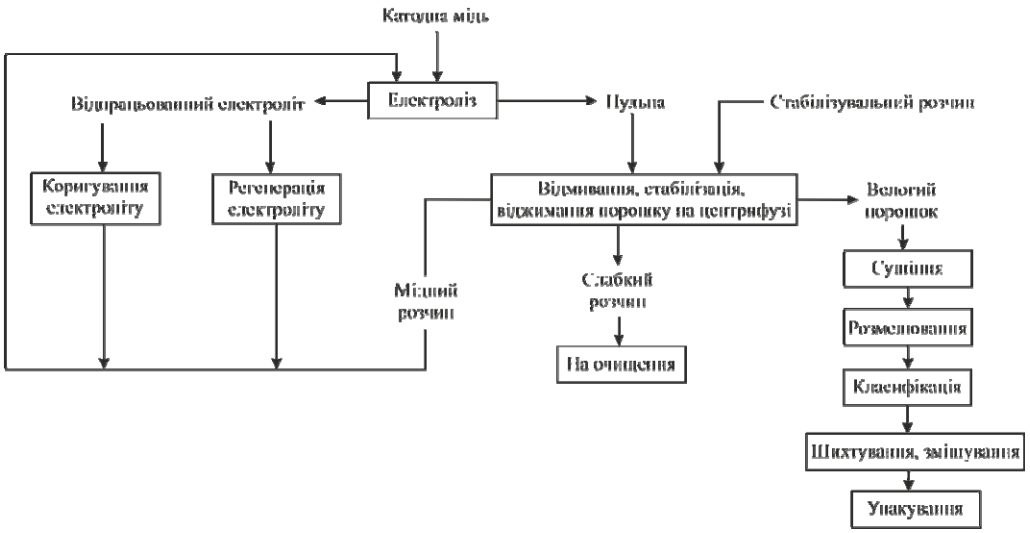

Figure 3. Chart of electrolytic method of receipt of copper powder [3]

Farther powder is dehydrated on centrifuges, warm up to the temperature 343 K for moving away of bits and pieces of electrolyte and wash hot water. The operation of stabilizing is carried out for prevention by oxidizations of powder. A stabilizator solution of milanetti (mixtures of insoluble in water organic acids and them sodium salts) serves as with a concentration 700...800 gs/l. Drying of powder execute for temperatures not higher, than 973 K (for prevention of oxidization of powder). The dried up powder is added to the grind, which is carried out in bullet mills; then during passing in a classifier through the set of сит, powder is divided into seven

brands depending on the sizes of particles. The different brands of powder mix up for the receipt of commodity powder homogeneous after composition and load in metallic drums, solder and order to composition or ship to the consumer.

After the electrowinning of copper powder a substantial role is played by surface-active matters (PAIR) which add to the electrolyte [4-10]. Research, that it is executed with the use of vinegar, salicylic, lemon alfano and sulfosalicylic acids [5] showed that during introduction to the electrolyte of lemon acid grainy dispersible powder was besieged. Addition of ac.a. results in enlargement of grains of sediment with more expressed crystalline structure, that it is related to diminishing in the ac.a. of COOH- of groups by comparison to three groups *COOH* in lemon acid. Adding of sulfosalicylic acid to the sulfate electrolyte assists besieging of powder with the globular structure of grains through a presence -CH_3, -*COOH*, -SO_3H but aromatic groups in acid.

It is set [4], that on quality of copper powder, got an electrolytic method, adding influences to the electrolyte of gelatin (G) and peg (PEG) as PAIR after in relation to the subzero concentration of blue vitriol in an electrolyte. Properties of the got copper powders and compositions of electrolytes are given in a table. 1.
microns

Table 1 – properties of the obtained copper powders [4]

Content of components of solution, g/l				Middle size of particles, microns	Content nanofactions, %
H_2SO_4	$CuSO_4$	G	PEG		
130	10	-	-	3...5	3...5
130	10	-	1,0	1...2	25...30
130	10	5,0	-	0,9...1	50...55

The most effective functional addition for diminishing of sizes of particles of powder is gelatin. In the case of his adding to the electrolyte the amount of particles of nanosizes increases considerably, and them a middle size is displaced to the nanoareas. It is related to that gelatin behaves to the group of additions which influence on speed of diffusion of rosacea ions, here is dispergating of particles of powder and rises him dentitst. An action of addition of peg is analogical, however an effect of increase of dispersion of particles of powder in this case is considerably less. It follows notices also, that during this concentration of basic elements of electrolyte, addition to gelatin results in smoothing of branches of dentitst. Such globular form of dentitst allowed after grinding to get powder which owns fluidity.

Adding to the electrolyte of glycerin causes the increase of his viscidity, assists some increase of expense of electric power, but here results in diminishing of size powder with the simultaneous increase of dentitst and diminishing of oxidization of powder [9]. Addition of ethylene glycol results in enlargement of grains of powder, diminishing of output after a current, to the sharp increase of dentitst powder at

besieging on a copper cathode, and also assists appearance of microcrystals of cube form at besieging on a steel cathode.

On quality of copper powder, that besiege, material and form of cathode [influences 9]. Dispersion of copper powders, depending on material of cathode, goes down in a row Al–Ti–X18H10T–Cu. A specific surface of powders, that it is got on aluminium and titanic electrodes, is more than on copper. More dendritic powders, than on a cathode from stainless steel, appear on aluminium and titanic cathodes. Such phenomenon conditioned by the features of crystallization of cathode sediment on a foreign surface.

Middle size of particles of powder, besieged on the cathodes of cylindrical form, more than on plates, here particles, that is besieged on a plate, have more ramified surface of dentitst.

Conclusions. For the receipt of copper powder which contains nanofactions, it is most expedient to apply an electrolytic method after which it is possible relatively easily to regulate the output of powder with the set properties, varying the closeness of current, composition of electrolyte, form and material of cathode, introduction to the electrolyte of PAIR.

Adding to the electrolyte of such PAIR as gelatin or peg increases the output of nanofactions of copper powder accordingly in 10 and 6 times. Use simultaneously of two additions, one of which owns a nglusucky action (for example, gelatin and benzotriazoles) allows to get more stable copper nanopowders chemically.

REFERENCES

1. **Тесакова, М. В.** Влияние добавок ультрадисперсных (наноразмерных) медьсодержащих порошков на трибологические свойства промышленных смазок [Текст] / М. В. Тесакова, В. И. Парфенюк, В. А. Годлевский // Электронная обработка материалов. – 2008. – № 6. – С. 56-62. – Библиошр.: с. 62.
2. **Волобуев, Н. К.** Влияние ультрадисперсных порошков металлов на свойства смазочных материалов [Текст] / Н. К. Волобуев, В. Д. Данилов, А. А. Кузнецов. – Трение и износ. – 1994. – Т. 15, № 5. – С. 871-876. – Библиогр.: с. 876.
3. **Набойченко, С. С.** Порошки цветных металлов [Текст] : Справочное издание / С. С. Набойченко, О. С. Ничипоренко, И. Б. Мурашова и др. – М.: Металлургия, 1997. – 542 с. – Библиография в конце каждой главы. – 1000 экз. – ISBN 5-229-01002-3.
4. **Внуков, А. А.** Особенности получения медных электролитических порошков с повышенным содержанием в них нанофракций [Электронный ресурс] / А. А. Внуков, Е. И. Демченко. – Режим доступа: http: //cyberleninka.ru/ article/n/osobennosti-polucheniya-mednyh-elektroliticheskih-poroshkov-s-povyshennym-soderzhaniem-v-nih-nanofrak-tsiy (дата обращения: 07.09.2015).
5. **Внуков, А. А.** Оптимизация факторов процесса электролиза с целью получения ультрадисперсного медного электролитического порошка [Электронный ресурс] / А. А. Внуков, И. Г. Рослик, Е. Э. Чигиринец. – Режим доступа: http://science.by/upload/iblock/a16/a1621a1731feb18bd7250602a2fed70b.pdf (дата обращения: 07.09.2015).
6. **Демеев, Б. Б.** Получение ультрадисперсных порошков меди электролизом в присутствии пав в электролите [Электронный ресурс] / Б. Б. Демеев, Р. А. Нурманова, Н. А. Калтаев, М. К. Наурызбаев. – Режим доступа: http:// bulletin.chemistry.kz/index.php/kaznu/article/view/199/140 (дата обращения: 08.09.2015).
7. **Кабацкая, В. В.** Оптимизация режима электролиза и состава электролита с целью получения медных порошков с повышенным содержанием в них нанофракций [Электронный

ресурс] / В. В. Кабацкая, А. А. Внуков, Е. Э. Чигиринец, И. Г. Рослик. – Режим доступа: //http://www.kpi. kharkov.ua/archive/ Наукова_періодика/vestnik /Хімія.хімічна_технологія. екологія/2010/47/21.pdf (дата обращения: 08.09.2015).
8. **Чигиринец, Е. Э.** Влияние режима электролиза и функциональных добавок в электролит на свойства и морфологию поверхности частиц медных электролитических порошков [Текст] / Е. Э. Чигиринец, И. Г. Рослик, А. А. Внуков // Вісник НТУ «ХПІ». – 2009. – № 21. – С. 15-20. – Библиогр.: с. 20.
9. **Байконурова, А. О.** Влияние добавок органических веществ на качество электролитического медного порошка [Текст] / А. О. Байконурова, Г. А. Усольцева, Р. С. Акпанбаев, О. Абушахман // Известия научно-технического общества «КАХАК». – 2011. – № 1 (31). – С. 35-39. – Библиогр.: с. 39.
10. **Fabricius, G.** The effect of additives on the electrodeposition of copper studied by the impedance technique [Текст] / G. Fabricius, G. Sundholm // J. Appl. Electrochem. – 1985. – №15. – P.797-801. – Bibliog.: p. 801.

Стаття надійшла до редакції
09.09.2015 р.
Рецензент, проф. І.Ф. Червоний