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Production of copper powder from electrolysis waste products

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Summary. The maximum value of hydrostatic pressure that is corresponding to the maximum value of erosion activity of acoustic field has defined. The technology for comminution of waste powder obtained during manufacturing of copper powder by electrolysis has been developed. The properties of electrolytic copper powder PMS-B treated in the ultrasonic field presented. A comparative analysis of structure and properties of copper powder before and after dispersion has been executed.

Key words: electrolytic copper powder, ultrasonic dispersion, ultrasonic device.

INTRODUCTION

The basic operations of production of the electrolytic copper powder are electrolysis, filtering for electrolyte removal, flushing, stabilisation, flushing, drying, comminution, sieving, mixing, control and packaging of powder. The waste powder with a particle size that is out of standard requirements sent on recasting in the metallurgical department [Kiparisov, Libenson 1980, Shatt 1983, Ryabicheva et al., 2010, Stoyanov, Shenkman 2010].

The remelting operation takes great expenses of electric power and considerable losses of material at all stages of the multioperation process. Therefore, development of recycling technologies of copper wastes which eliminating remelting operation is of great importance [Ryabicheva et al., 1998, Albano-Müller 1999, Ryabicheva, Tsirkin 2004, Kulu et al., 1999, Kiparisov et al., 1993]. Implementation of ultrasonic dispersion ensures high dispersity of powders of any hard materials. The highly efficient method is ultrasonic dispersion with application of increased hydrostatic pressure into the working chamber [Kiparisov, Libenson 1980, Agranat et al., 1987, Nikitin et al., 2011, Letunovskii et al., 1971].

OBJECTS AND PROBLEMS

The dispersion technology of any material depends on acoustic field parameters (frequency of ultrasonic oscillations source, amplitude of emitter displacement), physical and chemical properties of a fluid (density, saturation vapour pressure, chemical composition) and ambient conditions (hydrostatic pressure, temperature).

The hydrostatic pressure and temperature are making the most significant impact on dispersion process and cavitation damage.

The main purpose of this work is determination of hydrostatic pressure into the working chamber for ensuring the maximum erosion activity of acoustic field and investigation of its influence on changing the chemical, physical and technological properties of powder [Agranat et al., 1974].

Hydrostatic pressure in the working chamber of ultrasonic generator USVD-6 corresponding to the maximum value of erosion activity of acoustic field has defined on a basis of the ultrasonic cavitation theory. The erosion activity criterion of a single cavity was implemented for estimating of erosion activity of the acoustic field according to this theory [Agranat et al., 1974]:

$$\chi = \frac{R_{max}^3}{R_{min}^3 \Delta t f}, \tag{1}$$

where: f - is the frequency of ultrasonic vibrations; Δt - is the collapsing time within a cavitation pocket is changing of its radius from maximal R_{max} to minimal R_{min}.

The value of χ is always much higher then 1. The impact of acoustic field to substance is the more intensive, the higher value of erosion activity criterion. Simple and quite precise formulas for calculation of the maximum and minimum radius and collapsing time are using in engineering calculations for working fluids with viscosity values no more then 10^7 Pa·s [Agranat et al., 1974]:

$$R_{max} = \frac{0,4}{f}\left(1-\frac{P_0}{P_A}\right)\left(\frac{P_A}{\rho}\right)^{1/2};$$

$$R_{min} = \frac{1,2P_{\Pi}\left(1-\frac{P_0}{P_A}\right)\left(\rho P_A\right)^{-1/2}}{\left(2,9\frac{P_0}{P_A}-3,4\frac{P_0^2}{P_A^2}+3\frac{P_{\Pi}}{P_A}+0,6\right)f}; \qquad , \quad (2)$$

$$\Delta t = \frac{0,36}{f}\left(1-\frac{P_0}{P_A}\right)\left(2,9\frac{P_0}{P_A}-3,4\frac{P_0^2}{P_A^2}+0,6\right)^{-1/2}.$$

where: P0 - is the hydrostatic pressure; PA = ρcwA - is the acoustic pressure; ρ - is the fluid density; c - is the sound velocity into the fluid; w - is the angular frequency; A - is the generator displacement amplitude.

After substitution expressions (2) in (1) the equation (1) may be written in the following way:

$$\chi = \frac{8,14\left(P_A-P_0\right)^{5/2}\left(0,2P_A+P_0\right)^{7/2}}{P_A^3 P_{\Pi}^3}, \quad (3)$$

where: P_{Π} - is the saturation vapour pressure of fluid.

As appears from expression (3), a value of the erosion activity criterion χ for the given fluid defined by values of hydrostatic (P_0) and acoustic (P_A) pressures. The efficiency of ultrasonic impact is gradually increasing while growing of hydrostatic pressure [Agranat et al., 1974]. Supersonic waves are oscillating the cavitation bubbles. The size of bubbles increases and they are blasting with liberation of considerable quantity of energy while growing of hydrostatic pressure [Vasylkiv et al., 2005].

The extremum of function $\chi = \varphi(P_0)$ has found for hydrostatic pressure by calculating of relation P_0 and P_A which attaching a maximum value to criterion χ:

$$\frac{d\chi}{dP_0} = \frac{4,07}{P_A^3 P_{\Pi}^3}\left(P_A-P_0\right)^{3/2}\left(0,2P_A+P_0\right)^{5/2}\left(P_A-2P_0\right) = 0. \quad (4)$$

The calculations have provided for the following conditions - acoustic field parameters: frequency of ultrasonic oscillations 20 kHz (converter PMS15A-18 with 4 kilowatts output of generator USVD-6, power supply USG 2-10 [Kiparisov, Libenson 1980, Agranat et al., 1974, Letunovskii et al., 1971, Vasylkiv et al., 2005, Matsera et al., 1971]); amplitude of emitter displacement A = 2 µm. Physico-chemical properties of working fluid: saturation vapor pressure $P_{\Pi} =$ 0.0023 MPa; density $\rho =$ 1000 kg/m3; chemical composition is trisodium phosphate Na3PO4·12H2O with adding of surface-active substances with concentration of 20 kg/m3 and 5 kg/m3, respectively [Keller et al., 1977]. Ambient conditions: temperature of working fluid was 40°C [Hickling 1966]; hydrostatic pressure into the working chamber has been changed from 0.1 to 0.45 MPa. The results of calculations are presented on fig. 1.

The analysis of function $\chi = \varphi(P_0)$ has shown that maximum value of erosion activity criterion χ = 2.748.106 is corresponding to hydrostatic pressure of 0.22 MPa.

The acoustic field parameters presented above, physical and chemical properties of working fluid, temperature and calculated value of hydrostatic pressure equal to 0.22 MPa were used for ultrasonic dispersion of copper powder PMS-B with average particle size of 100 µm.

The working chamber of generator USVD-6 has filled with 2.5 cm3 of copper powder and aqueous solution of trisodium phosphate Na3PO4·12H2O with adding of surface-active substances and tightened. The pressure of 0.22 MPa created into the chamber by working gas. The volumetric ratio of hard phase to the fluid was equal to 1:4 [Agranat et al., 1974]. A necessary temperature into the working chamber has been ensured by means of regulation the water supply through the cooling jacket. The dispersion time was 20 minutes [Matsera et al., 1971]. The powder was unloaded into the container with perforated bottom and blown through by air at overpressure of 0.5 MPa during 5 minutes. The drying of powder has been conducted into the electric furnace with protective atmosphere at the temperature of 110°C.

Chemical, physical and technological properties of copper powder PMS-B GOST 4960-75 with average particle size of100 µm and copper powder dispersed by acoustic field have been defined using standard techniques. The content of copper was defined according to GOST 139381-

78; the oxygen content was fixed by weight loss of a powder portion after calcination into a hydrogen atmosphere; the granulometric composition was determined by GOST 18318-73; the bulk density was defined using GOST 199146-74; the compactibility was established pursuant to GOST 25280-82; the tap density was found by GOST 25279-82; the flowability was established in accordance with GOST 20899-75; the shape of particles has identified using optical microscope MIM-7; the microhardness has measured by microhardness-testing machine PMT-3; the picnometric density was determined according to the method presented in the paper [Kiparisov, Libenson 1980].

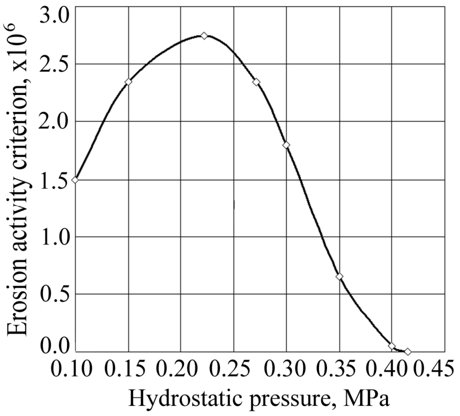

Fig. 1. Dependence of the erosion activity criterion on hydrostatic pressure

The oxygen content in the dispersed powder decreased from 0.10 to 0.08 % and the iron content remained constant (table 1).

Table 1. Chemical composition of copper powder PMS-B, %

Powder	Mass part		
	Cu	Fe	O
	Not less	No more	
Standard	99.5	0.02	0.10
Particle size >100 μm			
Dispersed	99.5	0.02	0.08

Decreasing of the oxygen content appeared due to destruction of non-uniform fragile oxide films that are suspended in the working solution at ultrasonic dispersion of powder. The interaction of powder particles with walls of working chamber is practically absent and powder pollution by extraneous substances, specifically by iron, is almost impossible. The percentage of dispersed powder with particle size less then 100 μm grew on 40 % according to results of comparative analysis (table 2). Internal stresses are appearing into material at ultrasonic impact and leading to diffusion-dislocation mechanism of fracture of plastic materials [Stepanov 2000, Anchev, Skakov 1974].

The fracture mechanism of destruction of plastic samples stipulated by formation of cluster from edge dislocations of one sign near the free surface, grain boundaries and surface of antinode of standing supersonic wave at the expense of dislocation climb from volume [Anchev, Skakov 1974]. The destruction occurs when the dislocation density into cluster reached of critical value. Particles of plastic metals are usually destroying on 3-6 parts during approximately 100 seconds [Stepanov 2000, Anchev, Skakov 1974].

Table 2. The granulometric composition of copper powder PMS-B

Powder	Granulometric composition					
	Content of particles, %, with size, mm					
	>0.224	<0.224	<0.140	<0.100	<0.063	<0.045
Standard	0,1	1	5-15	35-45	25-35	10-25
Particle size >100 μm	-	50-55	30-45	-	-	-
Dispersed	-	15-30	25-30	20-25	10-20	5-10

The dispersed powder demonstrated the highest bulk density, tap density and plasticity (table 3) due to powder parts have a smoothed surface (fig. 2). The pelletization of particles and cleaving of sharpen edges because of mutual friction and collisions of particles have taken place simultaneously with the dispersion process [Agranat et al., 1974].

Table 3. Properties of copper powder PMS-B

Powder	Bulk density, g/cm^3	Picnometric density, g/cm^3	Microhardness, kg/mm^2	Tap density, g/cm^3	Flowability, s
Standard	2,5	8,74	84	3,0	40
Particle size >100 μm	2,47	8,77		2,9	37
Dispersed	2,89	8,72	93	3,6	31

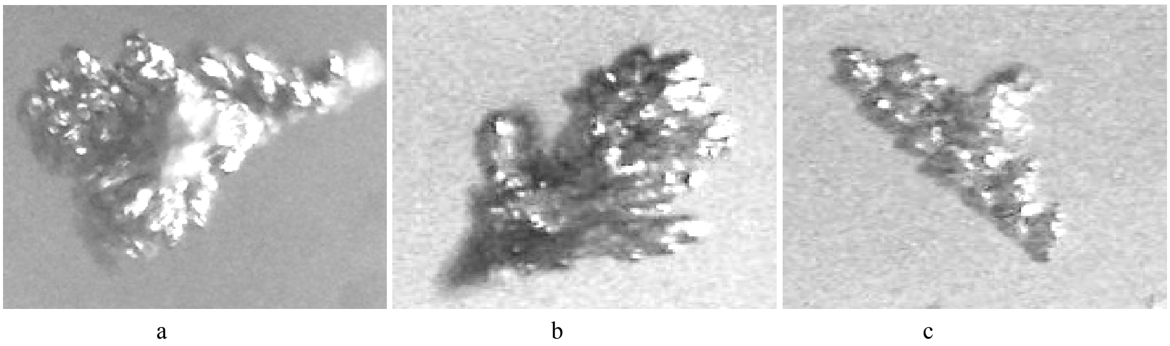

Fig. 2. The shapes of particles of PMS-B copper powder:
a – is the standard powder; b - is the powder with particle size >100 μm; c – is the dispersed powder, ×90

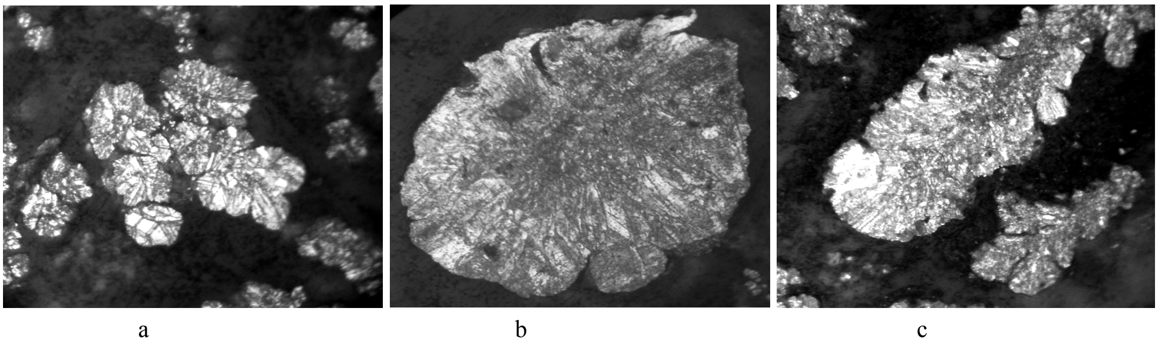

Fig. 3. The microstructure of copper powder PMS-B:
a – is the standard powder; b - is the powder with particle size >100 μm; c – is the dispersed powder, ×500

Furthermore, the ultrasonic impact leads to curing of surface defects in hard-phase systems due to considerable reduction of diffusive limitations [Tyapunina, Naimi 1999].

A slight decreasing of picnometric density of dispersed powder (table 3) observed due to presence of numerous imperfections and microcracks [Shatt 1983, Agranat et al., 1974].

The microstructure of powder particle before processing consists of small equiaxial grains in the middle part and much bigger grains directed from the centre to periphery (fig. 3, a). Such microstructure is the results of peculiarities of manufacturing process [Kozhanov et al., 1988]. The amount of large not equiaxial grains in a peripheral part of particles (fig. 3, c) was diminished gradually after dispersion. All bared butts between grains are wedging out at ultrasonic impact that leads to structural failure that characterised by development of the main crack at the grain boundaries [Agranat et al., 1974].

The mutual collisions of particles and increasing density of dislocations at the grain boundaries during dispersion leads to increasing of microhardness of particles, as the result of hardening [Matsera et al., 1971, Anchev, Skakov 1974], and takes an influence on declining the compactibility of copper powder (fig. 4).

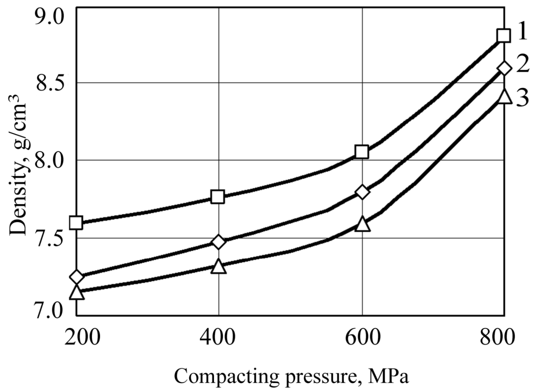

Fig. 4. The dependences of density of copper powder PMS-B from compacting pressure:
1 – is the standard powder;
2 - is the powder with particle size >100 μm;
3 – is the dispersed powder.

The areas of supersaturation of vacansions are appearing at ultrasonic dispersion of crystals near the grain boundaries and free surface. The condensation of redundant vacansions leads to formation of prismatic dislocation loops. The dislocation climb of edge dislocations from volume to crystal surface, grain boundaries and to a surface of antinode of standing wave are taking place at ultrasonic dispersion. The gradual increase in dislocations density (usually on 1-2 order) near free surface, grain boundaries and to a surface of antinode of standing wave observed as the result of such processes [Tyapunina, Naimi 1999, Polotskii, Bazeliuk 1970].

CONCLUSIONS

The value of hydrostatic pressure in the working chamber equal to 0.22 MPa has determined on a basis of ultrasonic cavitation theories for the following conditions: the ultrasonic oscillations frequency of 20 kHz and amplitude of emitter displacement 2 μm that allows production of dispersed powder.

The production technology of comminution of powder wastes that are appearing during production of copper powder by electrolysis that including powder dispersion on ultrasonic generator USVD-6, unloading from the working chamber, air blowing at overpressure and drying in furnaces into a protective atmosphere has been developed.

The percentage of fractions with particle size less then 100 μm in the dispersed powder increased on 40 % at processing of the electrolytic copper powder PMS-B in ultrasonic field during 20 minutes. The properties of powder produced by the proposed technology are meeting the requirements of standards.

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ПОЛУЧЕНИЕ МЕДНОГО ПОРОШКА ИЗ ОТХОДОВ ЭЛЕКТРОЛИТИЧЕСКОГО ПРОИЗВОДСТВА

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Аннотация. Определена максимальная величина гидростатического давления, которому соответствует максимальная величина эрозионной активности звукового поля. Разработана технология измельчения отходов в виде отсеянного порошка, которые образуются при производстве медного порошка электролизом. Представлены свойства медного электролитического порошка марки ПМС-В, обработанного в ультразвуковом поле. Выполнен сравнительный анализ порошка марки ПМС-В до и после диспергирования.

Ключевые слова: электролитический медный порошок, ультразвуковое диспергирование, ультразвуковая установка.