ABSTRACT

of the PhD thesis in specialty "6D072000- Chemical technology of inorganic substances" of **Nurtazina Aizhan Erkinbekkyzy**

on the topic "Development of an integrated technology for producing copper powder from complex electrolytes"

General characteristics of the work

The dissertation is devoted to the production of copper powder from aqueous solutions in the presence of organic ligands oxyethylidene diphosphonic ($C_2H_8O_7P_2$) and nitrilomethyltrienephosphonic ($C_3H_{12}NO_9P_3$) acids by electrolytic deposition, as well as the study of the physicochemical properties of the synthesized material. In the course of scientific work, the electrochemical behavior of divalent copper ions (Cu^{2+}) in the presence of organocomplex compounds in acidic and neutral environments was studied; The influence of main factors (such as changes in the concentration of copper ions in the electrolyte, pH, temperature, potential sweep rate) on the process itself is considered. At the same time, the shape and average particle size of the deposited copper powders were analyzed, and the maximum purity value was 99.54 wt.%. In addition, a vortex electrolysis installation was developed and its operability and efficiency were proven; A series of tests was carried out to obtain copper powder from an electrolyte containing an organic NTP complex, and the optimal process parameters with a current efficiency of 95.5% and a purity of 99.49 wt.% were identified. Along with this, the influence of deposition current density, temperature, concentration of copper ions, concentration of sulfuric acid and OEDP was studied. Using mathematical planning, a generalized process equation for a semi-industrial scale is derived.

Relevance of the research topic

Currently, electrolytic synthesis methods make it possible to obtain more than 60 types of metal powders. One of the most common and significant is definitely copper powder. According to a report published by the World Bureau of Metal Statistics (WBMS), global copper production in 2023 amounted to more than 27 million tons, and Kazakhstan ranks 11th in the world ranking of producing countries with 600 thousand metric tons. In this regard, the relevance of studying copper remains significant in our time. The process of electrodeposition of copper from acidic electrolyte solutions is widely used in industry for the production of printed circuit boards, protective and decorative coatings. Much interest is associated with studies of the initial stages of electrocrystallization of copper on substrates. Copper coatings are also widely used in technology: to give the surface a certain appearance, as well as a number of functional properties - electrical conductivity, protection against corrosion and against cementation of sections of steel products, ensuring adhesion of friction compositions to the steel base of clutch discs of automotive vehicles.

Despite the long history of research into copper electrodeposition, the information obtained about the laws of this process cannot be considered complete. This insufficiency is largely due to the fact that it is difficult to compare the results

of different studies. Thus, in the case of sulfate electrolytes, we are talking about solutions with different concentrations of copper sulfate, sulfuric acid and sodium sulfate. It is believed that sulfuric acid mainly affects the ionic strength and electrical conductivity of the solution, and also prevents the passivation of anodes and the formation of hydroxide compounds. The process of complexation of copper ions in solutions with a high concentration of sulfate ions, as well as the slowness of crystallization due to the occurrence of surface diffusion of the so-called ad-copper atoms, cannot be excluded.

At the moment, the requirements for new developments in the field of powder metallurgy have increased, primarily with regard to the exclusion of environmentally harsh and toxic substances from electrolytes, reducing the consumption of scarce and expensive materials, as well as increasing labor productivity and energy saving. From this point of view, the development of new high-performance, low-concentration and environmentally friendly electrolytes is of particular interest.

Recently, works have increasingly appeared in the literature in which organic substances are often used as additives in electrolytes to improve the properties of coatings and improve the electrolysis process, but such works are few. This paper presents the results of a study in solutions with the addition of NTP and OEDP, and also proposes the use of vortex electrolysis as a method for the electrodeposition of copper powder.

The purpose of the study

Synthesis of copper powder from organic complex electrolytes and optimization of the process of electrolytic production of copper on a laboratory and semi-industrial scale, including using mathematical planning methods.

Research objectives

1. Assess the influence of significant parameters on the electrochemical behavior of copper ions in the presence of complexing agents nitrilomethyltrienephosphonic ($C_3H_{12}NO_9P_3$) and oxyethylidene diphosphonic ($C_2H_8O_7P_2$) acids.

2. Synthesize copper powder from complex electrolytes and select optimal parameters for electrolysis with the highest product yield. Study the physicochemical properties of the obtained samples.

3. Design and assemble a vortex electrolysis installation. Select the most preferable characteristics for electrolytic deposition of copper powder from a complex electrolyte using vortex electrolysis, and also analyze the impact of the following factors: deposition current density, temperature, copper concentration, sulfuric acid concentration, NTP concentration, electrolysis duration.

4. Develop and test a schematic diagram of a pilot vortex electrolysis installation for producing copper powder on a semi-industrial scale (System volume is 30 liters).

5. Assess the contribution of each electrolysis parameter to the efficiency of copper powder formation using the mathematical planning method. Derive a generalized equation of the process. Determine the values of the functions that

provide the best conditions for the formation of copper powder on a semi-industrial scale.

Objects of research

Cu^0 powders, Cu^{2+} ions, nitrilotrimethylphosphonic acid, oxyethylidene diphosphonic acid.

Subject of research

Electrochemical behavior of copper ions and NTP, OEDP complexes, vortex electrolysis, technology for producing copper powder.

Research methods

When performing research on the topic of the dissertation work, the following methods were used: voltammetry, potentiometry, scanning electron microscopy, elemental analysis, spectrophotometry, gravimetry, and the method of multifactorial mathematical matrix planning.

The main provisions submitted for protection:

1) In an acidic environment in the presence of nitrilomethyltrienephosphonic acid ($C_3H_{12}NO_9P_3$), the highest current efficiency of copper was established at an NTF concentration of 7.5 g/l and amounted to 96.7%, and in a neutral environment the maximum CO occurs at an NTP concentration of 8 g/l and is 35%.

2) The addition of nitrilomethyltrienephosphonic acid ($C_3H_{12}NO_9P_3$) to the electrolyte increases the purity of copper powder by 1.2% and improves the physicochemical characteristics in comparison with electrolysis without NTP.

3) In an acidic environment in the presence of oxyethylidene diphosphonic ($C_2H_8O_7P_2$), the highest current efficiency of copper was established at a concentration of OEDP equal to 5 g/l and amounted to 96.8%, and in a neutral environment the maximum CO occurs at a concentration of OEDP of 10 g/l and is 40. 5%.

4) The vortex electrolysis installation provides a high CO of 95.5% and the production of fine copper powders with a particle size of 5-10 microns.

5) Current density has the greatest influence on the efficiency of formation of copper powder by vortex electrolysis.

Substantiation of the novelty and importance of the results obtained

The uniqueness of the doctoral dissertation lies in the comprehensive work carried out by the author of the study to study the properties of copper powder and obtain it from solutions of previously unused complex electrolytes NTP ($C_3H_{12}NO_9P_3$) and OEDP ($C_2H_8O_7P_2$); Optimal parameters for the synthesis of copper powder with the highest current efficiency have been proposed. An effective method of vortex electrolysis has been developed and experimentally tested on a laboratory and semi-industrial scale (with an electrolysis duration of 2.5 hours). The influence of the main factors on the electrodeposition process was studied, and the purity of the obtained copper powder samples was assessed (above 99%). Based on the data obtained, the use of mathematical planning was proposed to calculate the required functions (electrolysis conditions), which can replace 625 experiments using the empirical values of 25 experiments performed. Scientific novelty is also confirmed by a patent of the Republic of Kazakhstan.

Validity and reliability of the data obtained

The validity and reliability of the results is ensured by being based on standardized and correctly used methods, as well as metrological processing of the results of experimental studies. All results were processed using special licensed computer programs.

Theoretical significance of the results

The theoretical significance of the dissertation work lies in the fact that the results of the research part can be used for the electrochemical production of high-purity copper powder from a wider range of complex electrolytes of organic structure. The resulting complex with NTP or OEDP opens up the possibility of studying the electrochemical behavior of divalent copper ions and conducting electrolysis in a neutral environment, which in turn will create a favorable environmental effect due to the absence of the need to use concentrated sulfuric acid in large volumes, and will also simplify the requirements for the design of the electrolyzer. It is worth noting that in acidic solutions for NTP and OEDP it was possible to increase the efficiency of the process by 4-16% and the purity of the samples by 0.7-1.2%. In the course of voltammetric studies, a tendency to the formation of coatings was observed even at a current density of 500 A/m^2, which is the basis for the use of electrolytes based on OEDP as solutions for electrochemical copper plating. The developed vortex electrolysis installation has wide possibilities for changing the operating parameters of the process, which can also mark the beginning of new developments in this area. It is advisable to use a detailed analysis of the method of mathematical planning of an experiment and the derivation of the equation to select process conditions, excluding many operations. It follows from this that the research work of the dissertation candidate has a high degree of theoretical significance and can be taken as the basis for further research work and scientific projects in this area.

Practical significance of the results

The results of the presented scientific work on the development of technology for producing copper powder from complex electrolytes allow us to speak about the effectiveness and competitiveness of the proposed method. Optimization of the conditions for the electrolytic deposition of copper makes it possible to synthesize the final product of high purity. At the same time, the derived equation using the mathematical planning method makes it possible to determine the main parameters of electrolysis without the need for an experiment, which in turn has positive environmental and economic effects. Data from the dissertation work may be successful in commercialization. The target consumers of the results obtained include potentially interested private and public companies involved in copper production. These could be the largest copper producers in the country: Kazakhmys Corporation, KAZ Minerals, Eurasia Copper PLC LLP.

Compliance with the directions of science development or state programs (projects)

The dissertation work was carried out within the framework of the grant funding program of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan “Development of an integrated technology

for producing copper powder from complex electrolytes in a neutral environment" (Grant No. AP09058539).

Publications

The results of the work performed are reflected in three scientific papers, including:

- in an article in a peer-reviewed scientific publication in the scientific direction of the dissertation, indexed in the Science Citation Index Expanded of the Web of Science database (first quartile Q1) and having a CiteScore percentile in the Scopus database of at least fifty (74%);
- in an article published in a journal recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in a patent issued by the "National Institute of Intellectual Property" of the Ministry of Justice of the Republic of Kazakhstan.

Description of the doctoral student's contribution to the preparation of each publication

In the article "Obtaining of copper powder by method of a vortex electrolysis from acid sulphate electrolytes" (https://doi.org/10.1016/j.rineng.2022.100604) the author of the dissertation performed the experimental part of the work, conducted the primary analysis. The author of the thesis was directly involved in the interpretation of the results, and also participated in the writing of the initial and final versions of the text of the article.

In the article "Obtaining copper powder in the presence of nitrilotrimethylphosphonoic acid" (https://doi.org/10.32014/2021.2518-1483.93) Nurtazina A.E. is the first author. The doctoral student participated in the implementation of all experiments and the interpretation of the obtained results, was engaged in the description of the introduction, methodology, results, conclusion and design of drawings and graphs, independently engaged in the design of the article in accordance with the requirements of the journal.

In patent 32109 of the Republic of Kazakhstan: MPK S25S 5/02 "A method of obtaining copper powder" the dissertation candidate contributed to the preparation of the application according to the existing requirements, in adjustments, translation, and was also a correspondent.

Structure and scope of the dissertation

The dissertation consists of an introduction, 4 main sections, a bibliography comprising 167 references. The main text spans 97 pages excluding appendices, featuring 44 figures and 19 tables.