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## FORMATION OF ULTRADISPERSED COPPER POWDER IN THE CATHODIC SPACE

**Abstract.** The cathodic reduction of copper ions (II) with the formation of copper powders in sulphate solution over tetravalent titanium ions was studied.

It is shown that in copper sulphate (II) solution containing tetravalent titanium ions, the latter on the cathode in combination with copper ions (II) is reduced to form trivalent titanium. The titanium ions (III) formed in the cathode space immediately interact with copper (II) ions to form copper powders. Since this chemical reaction does not proceed on the cathode surface, there is no the further growth of the powder particles, and the reduced copper is formed as a dispersed powder. The ions of tetravalent titanium formed due to the chemical reaction are rereduced to the trivalent on the cathode and participate in the next act of the dispersed powder formation. Thus, in this process, the ions of tetravalent titanium act as a catalyst.

Thus, that part of the current, which in the known classical methods of the powder formation is completely consumed for hydrogen evolution, in this case when introducing the titanium (IV) ions into the solution, is consumed for its reduction and, in fact, for the formation of dispersed copper powder and, consequently the current yield is increased by 15-18%. The electron-microscopic method is used to determine the shape and size of the particles of the copper powders formed. It was found that in the absence of titanium (IV) ions in the electrolyte, the powders with sizes of 10-80 µm are formed in the electrolysis, and in the presence of titanium (IV), mainly 0.16-0.55 µm.

**Key words:** copper, titanium ions, powder, potential, anode, cathode, electrolyte, reduction, electrolysis.

In recent years, among the areas of metallurgy of nonferrous and precious metals, which are most rapidly developed and have a great prospect, powder metallurgy takes pride of place. Compared with the known methods of manufacturing complex shapes of metal parts, the method of powder metallurgy has a number of advantages. Firstly, this is almost complete non-waste technology, and secondly, the possibility of manufacturing various parts of the most complicated structures.

The growth in the production of metal powders is due to the fact that powder metallurgy allows creating fundamentally new materials with the specified composition, structure and properties.

At the present time, non-ferrous and precious metal powders are mainly produced by an electrochemical method, which makes it easy to regulate the process and produce a powder with various valuable properties [1-12].

Like for any technology, the determinant in powder metallurgy is the production of source raw materials, in this case it is the metal powder. In powder metallurgy, this technology segment determines not only the profitability of the entire production, but also significantly influences the structure and properties of the powders, and as a consequence, the scope of their application and the quality of the products.

Fine-dispersed copper powders have a number of properties, due to which they find application in many branches of engineering and industry. The high surface area of the powders, the branched dendritic shape of the particles, the oxidation stability, the electrical conductivity cause their use in the manufacture of various parts for electrical and engineering purposes, as well as in hydrometallurgy for the cementation

of rare and precious metals in the manufacture of lubricants. The spherical shape of copper powders is currently required in very large quantities in the development of 3D technologies.

Metal powders are produced by mechanical (cutting, grinding, sputtering of liquid metal) and physical-chemical (cementation, thermal decomposition of salts, autoclaving, electrodeposition) methods. Copper powders are mainly produced by electrochemical deposition [1, 2].

**Mechanism of the copper powder formation process.** Electrodeposition of metal powders is known to proceed at a current density higher than limiting one, with a sharp decrease in the concentration of discharging ions in the cathodic layer. Consequently, under these conditions, when the potential is shifted to the negative side, the discharge of hydrogen ions is the inevitable concomitant process and a part of the current is expended on this useless process. As a result, the current yield of copper powder is slightly below 100%, and in practice up to 30% of the current is expended on hydrogen evolution [1]. Thus, in the electrodeposition of a copper powder, two processes proceed on the cathode:



In the sulfate solution of copper (II), the chemical reaction of repropotioning may also proceed on the anode:



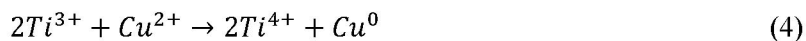
The consequence of reaction behavior (2) and (3) is imbalance of the cathode (below 100%) and anode (100-101%) processes, i.e. in the electrolyte there is a constant accumulation of copper ions [1, 3] and depletion of sulfuric acid. Within a day, as practice shows [2], the copper content in the electrolyte gradually increases. For extraction of excess copper, part of the electrolyte is sent to electrolysis in baths with insoluble lead anodes [1, 2], which is related to additional energy expenditures.

At first glance, it is practically and theoretically impossible to solve the problem of increasing the current yield of a copper powder in a fundamental way. We have shown for the first time [15] that intensification of the process of production of copper powder may be achieved by introducing titanium (IV) ions into the electrolyte.

In addition, it is known from the literature data [1, 2, 7] that metal powders are formed at high cathode current densities, i.e. when the limiting current density is reached, and newly formed copper crystals have time to grow, resulting in the formation of relatively large particles of metal powders. In this regard, it is believed that the production of ultradispersed nanosized metal powders directly on the cathode is practically impossible.

We have shown for the first time the principal possibility of producing ultradispersed and nanosized powders, i.e. fundamentally new methods for production of metal powder have been developed.

An increase in the current yield of copper powder, in our opinion, may be achieved by combining two processes: the direct discharge of copper ions by reaction (1) and the oxidation-reduction reaction (4):



The tetravalent titanium is introduced directly into the electrolyte and then, in addition to the reactions (1) and (2), the cathode undergoes its reduction.



The ions  $Ti^{3+}$  formed in the near-electrode space interact with copper (II) by reaction (4), due to proceed of which an additional amount of finely dispersed copper powder is formed and the current yield increases as a whole. The titanium (IV) ions are regenerated simultaneously, i.e. in this process, titanium (IV) acts as a catalyst.

The cathode reduction of copper (II) in the presence of Ti(IV) ions proceeds in several stages, and the process is carried out according to the following scheme (figure 1):

On the electrode surface and in the cathodic space, the following processes proceed:

- 1) diffusion of copper (II) ions to the cathode surface and its reduction;
- 2) diffusion of titanium (IV) ions to the cathode surface;

- 3) discharge of titanium (IV) ions, i.e. reduction to trivalent state;
- 4) diffusion of titanium (III) ions from the cathode surface;
- 5) oxidation-reduction reaction, i.e. interaction of the Ti (III) charge carrier formed on the surface of the cathode with copper (II) ions. These stages are further repeated cyclically.

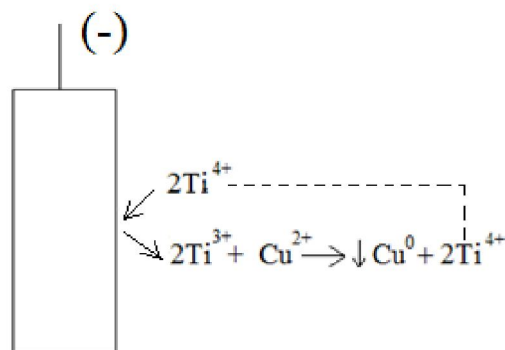


Figure 1 – Scheme of the formation of ultradispersed powders in the cathodic space in copper sulphate (II) solution in the presence of tetravalent titanium ions

Thus, that part of the current, which in the classical method of production of copper powder is consumed for hydrogen evolution, when titanium (IV) is introduced into the solution, is consumed for its reduction and, in fact, for the formation of a copper powder.

**Experimental technique.** Electrolytic production of copper powder was carried out in a cell with a capacity of 150 ml. The cathodes and anodes were made of electrolytic copper. Titanium (IV) was introduced as titanium sulfate. The formed copper powder was washed with water, stabilized with a soap solution to prevent oxidation, then dried and weighed. The shape and size of the powders were determined on a JEOL JSM-6610LV electron microscope.

**Experimental procedure.** The influence of the concentration of titanium (IV), copper (II), sulfuric acid and current density on the current yield (CY) of copper powder was studied.

The obtained experimental data confirmed the efficiency of the proposed process. When adding titanium (IV) ions, the current yield of copper powder increases by 15-18% depending on the current density, and at a titanium ion concentration higher than 4 g/l the current yield of copper powder practically does not change, i.e. dependence tends to saturation. In our opinion, this indicates the catalytic effect of titanium (IV) ions. Indeed, as seen from Figure 1, during the process, titanium (IV) is continuously regenerated, therefore, at its certain concentration, the conditions occur when the diffusion rate is no longer determined by the total concentration of titanium in the electrolyte, as regeneration of titanium (IV) ions completely ensures the maximum possible necessary concentration of trivalent titanium ions in the cathodic layer.

Interesting data were obtained when studying the influence of current density. In the presence of titanium (IV), with increasing current density, the current yield of copper powder decreases, as was to be expected, but its value is much higher than in the absence of titanium (IV). For example, at a current density of 5000 A/m<sup>2</sup> and in the absence of titanium ions, the current yield of the copper powder is 53.2%, and in the presence of titanium ions it is 83.4%. Consequently, the speed of the process may be dramatically increased without reducing the current output.

Laboratory experiments served as the basis for testing this method on a large-scale laboratory installation. These experiments were carried out in an electrolytic bath with a capacity of 1.0 liters. Model electrolyte was undergone to electrolysis. The experiments were carried out at a cathodic current density of 3000 A/m<sup>2</sup>, with a circulation rate of 0.5 l/h. The results are shown in figure 2. As seen, in the presence of titanium (IV) ions, the current yield of the copper powder increases on average by ~16%, and the mass of the produced powder increases by 5.9 g.

Thus, the results obtained make it possible to conclude that the proposed method for producing finely dispersed copper powder is distinguished by high efficiency and simplicity. The latter circumstance is due to the fact that the electrolytic production of copper powder may be carried out in operating electrolysis baths, and special preparation of production is not required.



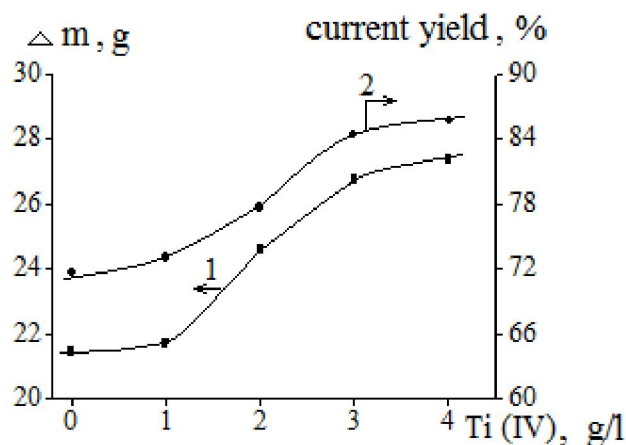
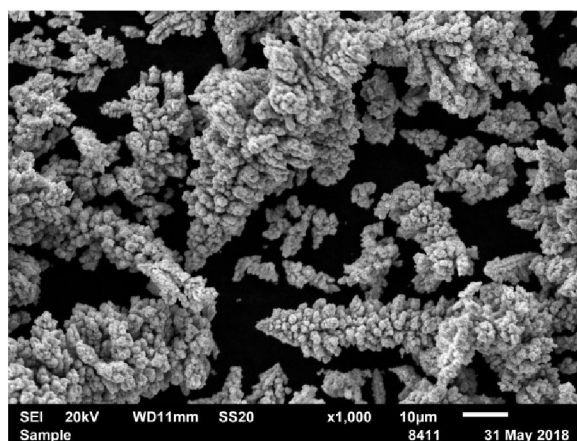
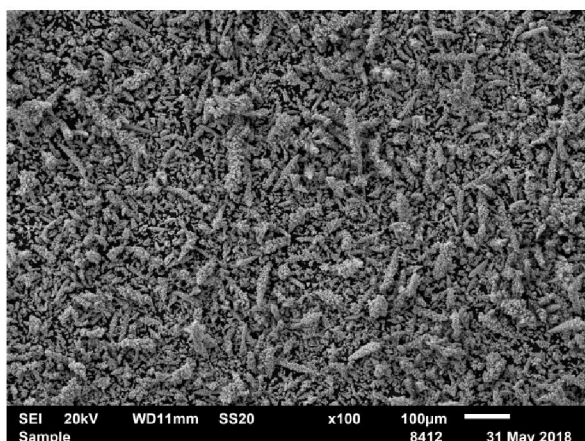
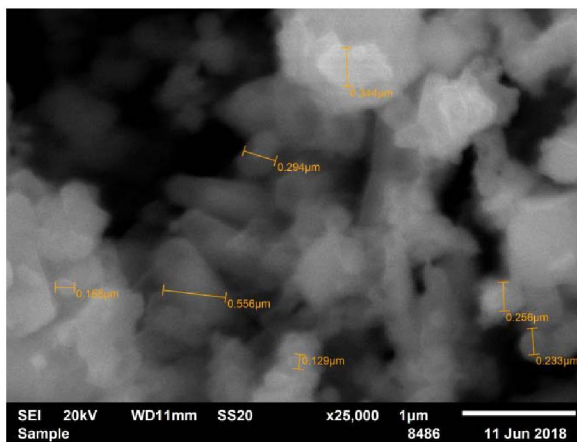
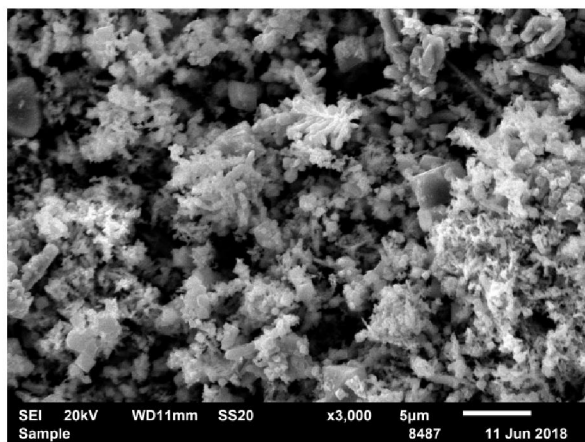


Figure 2 –  
Influence of the concentration of titanium (IV) ions  
on the current yield and on the amount of powders formed  
when performing large-scale laboratory tests:  
(the composition of the electrolyte Cu (II) is 12.0 g/l,  
Ti (IV) is 4 g/l, the cathodic current density is 3000 A/m<sup>2</sup>,  
the circulation rate is 0.5 l/h, the temperature is 25°C,  
the duration – 3 hours)

We have studied the shape and sizes of the particles of copper powders produced under various conditions of electrolysis by electron-microscopic method. As seen from figure 3, the copper powders produced in the presence of titanium (IV) ions and in their absence differ sharply. Powders produced in the absence of titanium (IV) ions have an elongated dendritic appearance with different outlines and particle sizes within 10-80 μm (figure 3a), and in the presence of titanium (IV), ultradispersed powder are formed. There is a small amount of dendritic particles with a size of about 3 μm and mainly powders of a spherical shape with particle sizes within 0.16-0.55 μm are formed (figure 3b).



a)



b)

Figure 3 – Microphotographs of copper powder:  
a - produced in the absence of titanium (IV) ions; b - produced in the presence of titanium (IV) ions

It should be noted that since the reaction of copper powder formation according to reaction (3) proceeds not on the surface of the cathode, but in the cathodic space, there is no the further growth of the particles. In this regard, the reduced copper (II) ions are mainly formed as an ultradispersed powder.

**Conclusions.** Due to the fact that part of the current, which in previously known methods for production of the powder is consumed for hydrogen evolution, when introducing the titanium (IV) ions into the solution, is consumed for its reduction and, in fact, for the formation of ultradispersed copper powder, the current yield is increased, because the rate of discharge of hydrogen ions decreases and the dispersion increases.

In conclusion, we would like to note once again that dispersed metal powders produced by electrochemical methods have become indispensable raw materials in various industries. For example, nanosized copper powders are used as catalysts in organic synthesis reactions, as a cement agent when extracting precious metals from waste solutions, for the production of porous bronze-backed bearing, etc. In recent years, nanosized spherical shapes of metal powders have been widely used in the creation of 3D technology.

It should be noted that in hydrometallurgical processes of gold and silver production a relatively large amount of precious metals is lost with industrial and waste waters. According to the existing technology, precious metal ions from aqueous solutions are extracted mainly by cementation by iron turnings. In this case, most of the cement agent in the form of iron is consumed in an undesirable process - the reduction of hydrogen ions, as well as the emission of a very toxic gas - arsine (since arsenic is present in solutions formed in the processing of gold-bearing solutions), i.e. there is a mortal danger for operating personnel.

Another industry that uses dispersed metal powders is the production of lubricants [16]. For example, it was very simple and convenient for steel surfaces to use lubricants containing finely dispersed copper powder allowing to eliminate wear. The discovery of the wearproof effect is of particular importance due to economic efficiency. Thus, increasing the wear-resistance of machines only by 2-3 times brings the national economy 5-6 billion rubles in savings per year [16]. When using ultradispersed copper powders, the wear-resistance of the parts may be increased to an even greater degree. It is shown that the use of metal plaque (containing very fine copper particles) lubricants for the chassis units of only one car gives a saving of up to 280 rubles per year (according to data of 1988).

In view of the aforesaid, the development of methods for producing ultradispersed copper powder and its application for the extraction of precious metal ions completely eliminates the irretrievable loss of precious metals with industry waters. In addition, the use of metal powders as a wearproof lubricant is an urgent task and has both practical and theoretical significance.

Currently in the CIS there is only one shop for the production of copper powder, which is located in Verkhnyaya Pyshma, Sverdlovsk Oblast (Russia), where about 10-15 thousand tons of this product are produced per year. The average size of copper powder particle is 50-70  $\mu\text{m}$ . Unfortunately, copper powders with these particle sizes do not meet all the requirements currently imposed on them.

The novelty of the method for producing ultradispersed copper powder is patented [15]. At the present time, we are studying the process of formation of copper powder in the cathodic space [17], as well as in the interelectrode space [18].

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### КАТОД АУМАҒЫНДА УЛЬТРАДИСПЕРСТІ МЫС ҰНТАҚТАРЫНЫҢ ТҮЗІЛУІ

**Аннотация.** Құрамында төрт валентті титан иондары бар күкірт қышқылы ерітіндісінде, мыс (II) иондарының мыс ұнтақтарын түзе тотықсыздануы зерттелді.

Күкірт қышқылды мыс (II) ерітіндісінде төрт валентті титан иондары болған жағдайда, кейінгі ион мыс (II) иондарымен бірге катодта үш валентті титан иондарына дейін тотықсызданатыны көрсетілді. Түзілген титан (III) иондары катодауағында бірден мыс (II) иондарымен әрекеттесіп мыс ұнтақтары түзіледі. Бұл химиялық реакцияның жүруі катод бетінде емес болғандықтан, түзілген мыс бөлшектерінің ары қарай өсуі іске аспайды, сол себепті өте дисперсті мыс ұнтақтары түзіледі. Химиялық реакция нәтижесінде түзілген төрт валентті титан иондары қайтадан үш валентті күйге дейін тотықсызданып, қайтадан мыс (II) иондарымен әсерлесіп дисперсті мыс ұнтақтары түзіледі. Демек, бұл жағдайда төрт валентті титан иондары катализатор рөлін атқарады.

Қорыта айтқанда, мыс ұнтағын белгілі классикалық әдістермен алған кезде электр тоғының сутегінің бөлінуіне кететін бөлігі, біз ұсынған әдісте, титан (IV) иондарын электролитке қосқан кезде, кейінгі ионның тотықсыздануына және нақты айтар болсақ дисперсті мыс ұнтақтарының түзілуіне жұмсалады. Нәтижесінде мыс ұнтақтарының түзілуінің ток бойынша шығымы 15-18 %-ға өседі.

Түзілген мыс ұнтақтары бөлшектерінің өлшемі мен пішіні электронды-микроскоп әдісі арқылы анықталды. Электролизді жүргізу барысында электролитте титан (IV) иондары жоқ кезде бөлшектерінің өлшемі 10-80 мкм болған ұнтақтар, ал титан (IV) иондары бар кезде – өлшемі 0,16-0,55 мкм болған ұнтақтар түзілетіндігі анықталды.

**Түйін сөздер:** мыс, титан иондары, ұнтақ, потенциал, анод, катод, электролит, тотықсыздану, электролиз.

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### ФОРМИРОВАНИЕ УЛЬТРАДИСПЕРСНОГО МЕДНОГО ПОРОШКА В ПРИКАТОДНОМ ПРОСТРАНСТВЕ

**Аннотация.** Исследовано катодное восстановление ионов меди (II) с образованием порошков меди в сернокислом растворе в присутствии ионов четырехвалентного титана.

Показано, что в сернокислом растворе меди (II), содержащем ионы четырехвалентного титана, последний на катоде совместно с ионами меди (II) восстанавливается с образованием трехвалентного титана. Образующиеся в прикатодном пространстве ионы титана (III) сразу же взаимодействуют с ионами меди (II) с образованием медных порошков. Так как эта химическая реакция протекает не на поверхности катода, дальнейший рост частиц порошка не происходит и при этом восстановленная медь формируется в виде дисперсного порошка. Образованные за счет химической реакции ионы четырехвалентного титана вновь восстанавливаются до трехвалентного на катоде и участвуют в следующем акте образования дисперсного порошка. Таким образом, в данном процессе ионы четырехвалентного титана выступают в качестве катализатора.

Таким образом, та часть тока, которая в известных классических способах получения порошка полностью расходуется на выделение водорода, в данном случае при введении ионов титана (IV) в раствор, расходуется на его восстановление и фактически на образование дисперсного медного порошка и, как следствие повышается и выход по току на 15-18 %. Электронно-микроскопическим методом определены форма и размер частиц образовавшихся порошков меди. Выявлено, что в отсутствии в электролите ионов титана (IV) при электролизе формируются порошки с размерами 10-80 мкм, а в присутствии титана (IV) в основном – 0,16-0,55 мкм.

**Ключевые слова:** медь, ионы титана, порошок, потенциал, анод, катод, электролит, восстановление, электролиз.

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