

BULLETIN OF NATIONAL ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN

ISSN 1991-3494

Volume 6, Number 376 (2018), 6 – 10

<https://doi.org/10.32014/2018.2518-1467.21>

UDC 541.13/ 621.762

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FORMATION OF DISPERSE COPPER POWDER IN ANODIC SPACE IN SULFURIC ACID SOLUTION

Abstract. The proposed article considers the dissolution of a copper electrode in the anodic polarization of a metal in the presence of a $\text{Ti (IV)} \leftrightarrow \text{Ti (III)}$ catalyst system and the formation of an ultradisperse powder that have passed into a solution of copper (II) ions. Electrolysis was carried out under standard conditions in a sulfuric acid medium in an electrolyser with unshared spaces using DC. During the anodic polarization of copper electrodes copper ions (II) are formed. The copper (II) ions transferred to solution on the anode surface are reacted with titanium (III) ions to form a nanosized copper powder. As a result, a solution of colloidal copper is formed. The oxidized titanium (IV) ions diffuse in the direction of the cathode and are reduced to the trivalent state. It is shown that the ions of trivalent titanium reduce the ions of divalent copper formed at the anode to a nanoscale metal powder. Thus, in the course of electrolysis, titanium ions in the electrolyte form act as a continuous catalyst system. It is established that the stability formed in the anode space during electrolysis of solutions of colloidal copper varies with the concentration of titanium (III) ions.

Key words: copper, powder, electrolysis, titanium, catalyst, electrode, cathode, anode.

In the production of modern techniques copper powder is in great demand [1-5]. Copper powder is used in the welding technique for the alloy, in the work of special cutting, in the preparation of lubricants. Dispersed copper powders are used in various branches of technology and industry, in particular, for the manufacture of products in the electrochemical, automotive industries, as well as for the production of high-quality plating metallic lubricants with a wear-free effect.

Recently dispersed copper powders of spherical shape are widely used in 3D technology.

Metal powder can be obtained in different ways. They are divided into mechanical, physicochemical, hydroelectrometallurgical methods and a method of spraying [6–9]. And the process of obtaining nanosized copper powder through electrolysis is still poorly understood. Therefore, the study of the influence of various parameters on the process of obtaining and the formation of copper powder through electrolysis is of great importance.

According to literature sources, the bulk of copper powder is obtained by electrochemical methods [10]. All processes of copper powder production are well studied [11-15]. The dimensions of the copper powder obtained by the known method is 40-100 micrometer. And the problems of obtaining metal powders of dispersed and nano-size remain open. Various scientific studies are carried out to develop a rational method for producing ultrafine copper powder. Our early research works prove that the formed copper powders obtained with the participation of electrolysis with titanium ions (IV) and alternating currents have smaller sizes [16, 17].

With the participation of alternating current, copper (II) ions are oxidized in the cathode period to a metal powder, and in the anode period slightly dissolves and dispersion increases, large parts are ground and eventually copper powders of 0.1-0.3 μm are formed.

The possibility of obtaining ultrafine copper powder in the cathode part using the catalytic system $\text{Ti (IV)} \leftrightarrow \text{Ti (III)}$ indicated in early writings of professor Baeshov A. [18-20]. Our detailed studies have shown that the copper powders formed during the cathodic oxidation of copper (II) ions at high current density immediately grow in size after formation. As a result, it became known about the impossibility of obtaining dispersed copper powder by a known electrochemical method.

In earlier research work indicated the possibility of obtaining dispersed copper powder on the surface of the copper anode and secured this discovery patent of the Republic of Kazakhstan [20]. In the proposed work showed the possibility of such processes in a simple electrolysis with indivisible electrode spaces.

Electrolysis is carried out in an electrolyzer of 150 ml, made of Plexiglas. A copper electrode is used as the anode, and a titanium electrode as the cathode. As part of the electrolyte used sulfuric acid solution with ions of three and tetravalent titanium. It should be noted that copper ions are absent in the solution. During electrolysis, the formation of fine copper powder on the surface of the copper anode was observed. The number of copper powders formed using the current is affected by the current density, the concentration of titanium (III) ions and sulfuric acid in the electrodes.

During electrolysis, the formation of copper powder occurs by the following mechanism:

The reaction scheme that occurs in the electrodes is shown in figure 1.

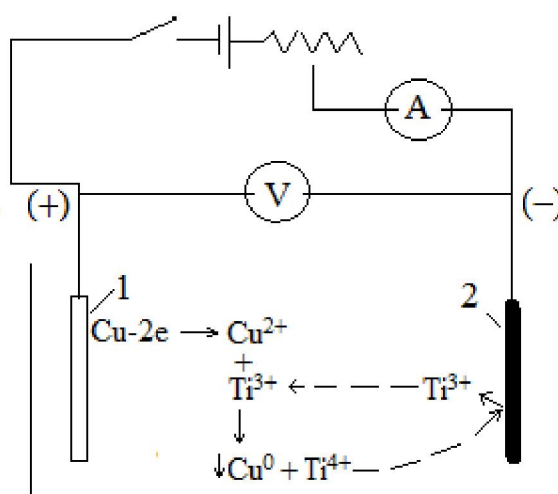


Figure 1 – Schematic diagram of the electrolyzer.

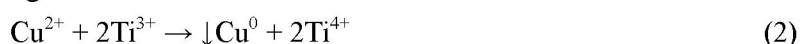
The scheme of reactions occurring in the electrodes and electrolytes:

1 – copper electrode; 2 – titanium electrode

With anodic polarization of the copper electrode, it dissolves while forming its own ions:



The formed copper (II) ions interacting with titanium (III) ions on the surface of the anode to form copper powders. As a result, the following chemical reaction occurs on the anode electrode:



And Ti (IV) ions formed as a result of reaction (2) diffuse in the direction of the cathode and dissolve in the cathode to the trivalent state:



The ions Ti (III) formed as a result of the reaction (3) are differentiated in the direction of the anode and re-interacting with the ions of copper (II) formed in the anode according to the reaction on the anode area to form a copper powder. These reactions during the electrolysis are repeated by cycle.

In the present article the influence of different parameters on the mechanism of copper powder formation is studied.

Electrolysis with the composition of sulfuric acid 50g/l titanium (III) 4 g/l and 2 g/l titanium (IV) is carried out and the effect of the current density in the electrodes is studied.

The amount of copper powders formed during electrolysis was determined by the solubility of the copper anode. Since it became known that copper (II) ions formed in the anode and titanium ions (III) formed on the electrode surface interacting with each other form a colloidal solution with the content of fine copper powder. After 60-90 minutes, the stability of this colloidal copper solution decreases and settles on the bottom of the electrolyzer in the form of an ultrafine powder. According to our calculations, the constant value of the "red-ox" process occurring during the reaction (2) is $\sim 10^{10}$. This shows that copper (II) ions formed in the anode and titanium(III) ions included in the solution are fully involved in the reaction.

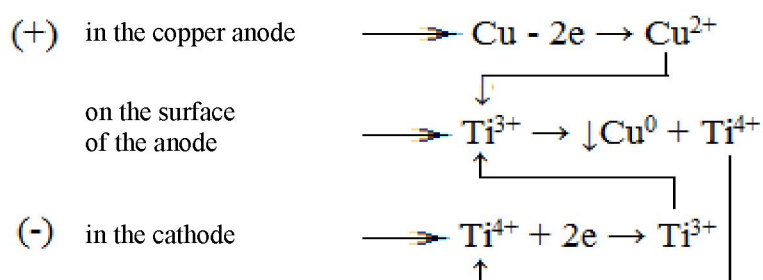
This means that copper (II) ions formed in the anode are fully involved in the formation of colloidal copper powder. As the current density in the electrodes increases to 100 A/m^2 , it can be assumed that colloidal copper powder is formed up to 100%.

When the concentration of titanium ions (III) varies in the range of 1-4 g/l, copper ions (II) formed in the anode through a complete reaction (2) form a solution of colloidal copper powder.

It is observed that with an increase in the concentration of titanium ions(III), the stability of the colloidal copper solution decreases. For example, at the concentration of titanium ions (III) 1 g/l stability of colloidal copper solution is more than 180 minutes. Only after a certain time, the formed copper powders of nanosizes interact with each other as nano particles settle to the bottom of the electrolyzer.

With the concentration of sulfuric acid in the range of 50-150 g/l in the formation of colloidal copper solution and in the volume of the powder, no change was observed.

As a result of the study, it was proved that during electrolysis, the reactions on the electrode surface and the anode area occur according to the following scheme:



At the end of the practice, the particles of the formed copper powders were studied and the shapes and sizes were determined. With the help of a scanning electron microscope, a snapshot of the copper powder was taken, magnified up to 50,000 times (figure 2). According to the figures (figure 2 of the scheme a, b), it can be determined that the particle sizes of the powder are almost the same. Only in some places small particles together created a large volume. The current size of the resulting copper powder can be observed in the increased to 50,000 times figure 2 g-image. The particle sizes are almost identical, in the range of $0.097\text{-}0.123 \text{ }\mu\text{m}$. It is concluded that these dimensions were formed as a result of the combination of nanosize powders.

In the result of the study it was determined that with $\text{Ti(IV)} \leftrightarrow \text{Ti(III)}$ catalytic system involving direct current, normal condition, sulfuric acid medium, in electrolysis without dividing the surface of the electrodes on the surface of the anode is obtained copper powder with the nanoscale. That is, based on specified parameters, from any of the copper electrode with the participation of ions of trivalent titanium, dissolving the anode in the area of the anode can be obtained colloidal copper solution with nano-sizes metal and this is demonstrated for the first time. It is also indicated for the first time that in this case chemical and electrochemical reactions occur simultaneously.

In conclusion, would like to note that the proposed research results based on experiments show the production of very fine copper powders using a new mechanism on the anode surface or on the anode area.

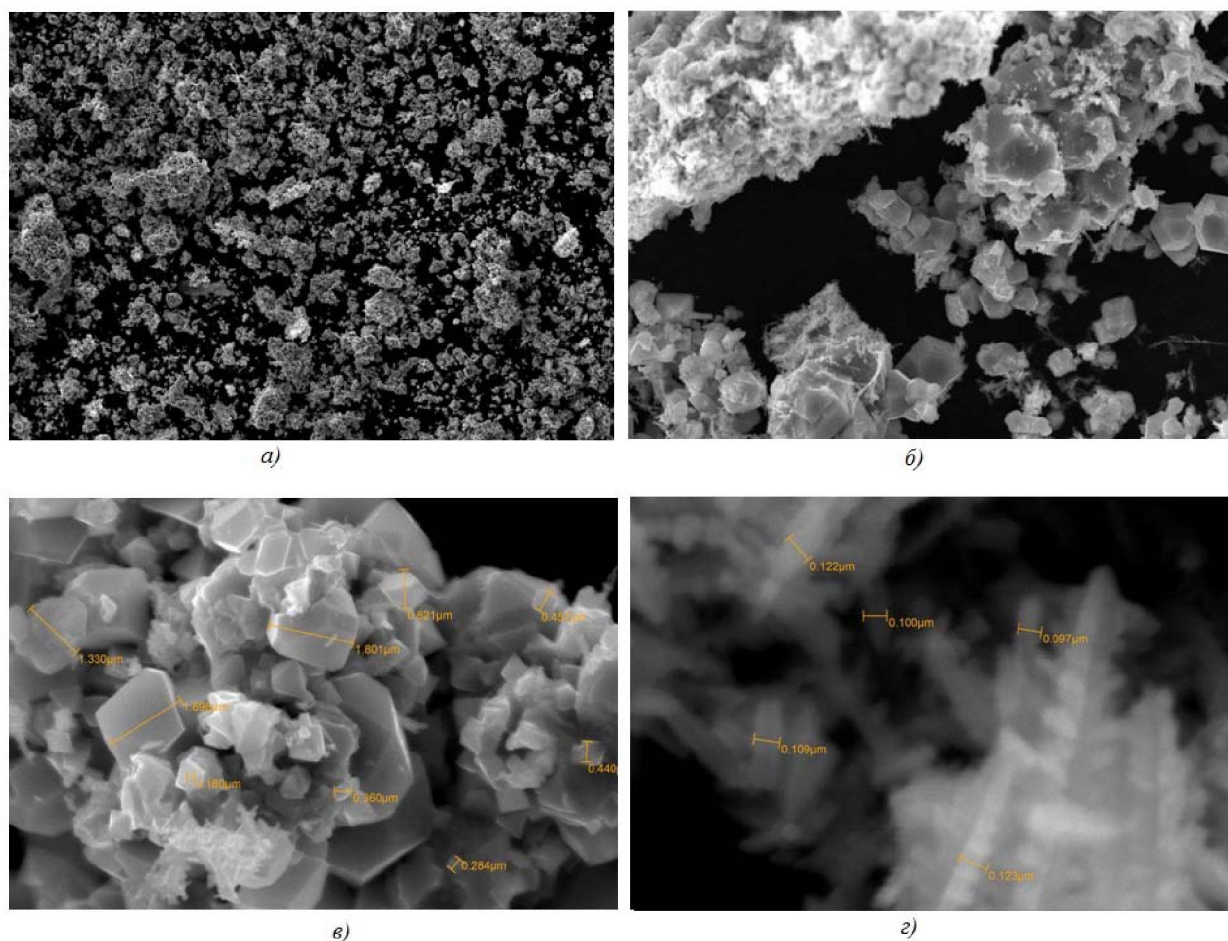


Figure 2 – Microscopic image of copper powders formed on the anode area:

a) increased up to 300 times; b) increased up to 3000 times;
c) increased up to 10,000 times; d) increased up to 50,000 times

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КҮКІРТ ҚЫШҚЫЛДЫ ЕРІТІНДІДЕ ДИСПЕРСТІ МЫС ҰНТАҚТАРЫНЫҢ АНОД КЕҢІСТІГІНДЕ ТҮЗІЛУІ

Аннотация. Ұсынылып отырған мақалада $Ti(IV) \leftrightarrow Ti(III)$ каталитикалық жүйеде мыс электроды анодты поляризацияланғанда металдың еруі және еріген мыс (II) иондарынан өте дисперсті ұнтақтың түзілуі қарастырылды. Электролиз тұрақты ток қатысында, қалыпты жағдайда, күкірт қышқылды ортада, электрод кеңістіктері бөлінбеген электролизерде жүргізілді. Мыс электродын анодты поляризациялағанда мыс (II) иондары түзіледі. Ерітіндіге өткен мыс (II) иондары сол сәтте анод бетінде титан (III) иондарымен әрекеттесіп наноразмерлі мыс ұнтағына дейін тотықсызданады. Нәтижесінде коллойдты мыс ерітіндісі қалыптасады. Тотыққан титан (IV) иондары катод бағытына қарай диффузияланып, үш валентті күйге дейін тотықсызданады. Үш валентті титан иондары, анодта түзілген мыстың екі валентті иондарын қайта наноразмерлі метал ұнтағына дейін тотықсыздандырып отыратындығы көрсетілді. Электролит құрамындағы титан иондары электролиз кезінде осылайша өзінің үздіксіз каталитикалық қызметін атқарады. Электролиз нәтижесінде анод кеңістігінде түзілген коллойдты мыс ерітіндісінің тұрақтылығы, титан (III) иондарының концентрациясына байланысты өзгеретіндігі анықталды.

Түйін сөздер: мыс, ұнтақ, электролиз, титан, катализатор, электрод, катод, анод.

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ФОРМИРОВАНИЕ ДИСПЕРСНОГО МЕДНОГО ПОРОШКА В АНОДНОМ ПРОСТРАНСТВЕ В РАСТВОРЕ СЕРНОЙ КИСЛОТЫ

Аннотация. В предлагаемой статье рассмотрено растворение медного электрода при анодной поляризации металла в присутствии каталитической системы $Ti(IV) \leftrightarrow Ti(III)$ и формирование ультрадисперсного порошка, перешедших в раствор ионов меди (II). Электролиз проводили при стандартных условиях в сернокислой среде в электролизере с неразделенными пространствами с применением постоянного тока. При анодной поляризации медных электродов образуются ионы меди (II). Перешедшие в раствор ионы меди (II) на поверхности анода взаимодействуя с ионами титана (III) восстанавливаются с образованием наноразмерно порошка меди. В результате формируется раствор коллоидной меди. Окисленные ионы титана (IV) диффундируют в направлении катода и восстанавливаются до трехвалентного состояния. Показано, что ионы трехвалентного титана восстанавливают образующиеся на аноде ионы двухвалентной меди до наноразмерного порошка металла. Таким образом, при электролизе ионы титана, находящиеся в составе электролита выступают в качестве непрерывной каталитической системы. Установлено, что устойчивость, образованных в анодном пространстве при электролизе, растворов коллоидной меди меняется в зависимости от концентрации ионов титана (III).

Ключевые слова: медь, порошок, электролиз, титан, катализатор, электрод, катод, анод.

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