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PATTERNS OF FORMATION OF DISPERSED COPPER POWDERS IN THE BODY OF ELECTROLYTE DURING THE USE OF COPPER ANODE IN SULFURIC ACID SOLUTION ALONG WITH TITANIUM (IV) IONS

Abstract. For the first time it was shown that when a copper-titanium pair of electrodes is polarized in a solution of sulfuric acid with titanium (IV) ions, copper powders are formed between the holes of the electrodes.

The mechanism of formation of copper powders during electrolysis is investigated. It was shown that during the polarization of copper and titanium electrodes in a solution of sulfuric acid with Ti (IV) ions, copper anodes dissolve, forming copper (II) ions, and in the cathode titanium (IV) ions are oxidized to the tri-valent state. At this time, the color of the electrolyte at the cathode is purple, and at the anode it turns blue. It was established that the formed copper (II) and Ti (III) ions are found in the main gap of the electrodes, as a result of which nano-scale copper powders are formed.

It was shown that the resulting tetra-valent titanium ions in the cathode are again oxidized to the tri-valent state, interacting with copper (II) ions. Copper powders form again between the electrodes, and these processes are repeated cyclically. It was shown that during the electrolysis between the electrodes colloidal copper powders are first formed, and then they are combined and are precipitated.

Key words: titanium ions, copper, powders, electrolysis, electrolyte, reduction.

Introduction. Dispersed copper powders have a special property. Therefore, copper powders are used in various fields of production. Electrochemical methods have been widely used in the preparation of copper powders. The patterns of the formation of copper powders during cathodic polarization have been studied in detail [1-18].

In our previous research, we were the first in the world to show that when electrolysis is performed using copper electrodes in a solution of sulfuric acid with four-valent titanium ions, copper powders are formed between the electrodes and the discovery was protected by the patent of the Republic of Kazakhstan [17].

This article describes the impact of current density, sulfuric acid in solution, concentrations of titanium (IV) ions and the duration of electrolysis on the current consumption (CC) of the formation of dispersed copper powders. Copper was used as the anode electrodes, and titanium plates as the cathode. The area of the electrodes is equal to 3 cm², the distance between them is 6 cm. A solution of sulfuric acid was used as the electrolyte. It stands to mention that the electrolyte contains no copper ions. The principal variant of the electrolyzer and the reactions taking place in it is shown in Figure 1.

Theoretical. During electrolysis, the formation of copper powders is carried out by the following mechanism: when polarizing copper and titanium electrodes in a solution of sulfuric acid with Ti (IV) ions, the copper anode dissolves forming copper (II) ions:



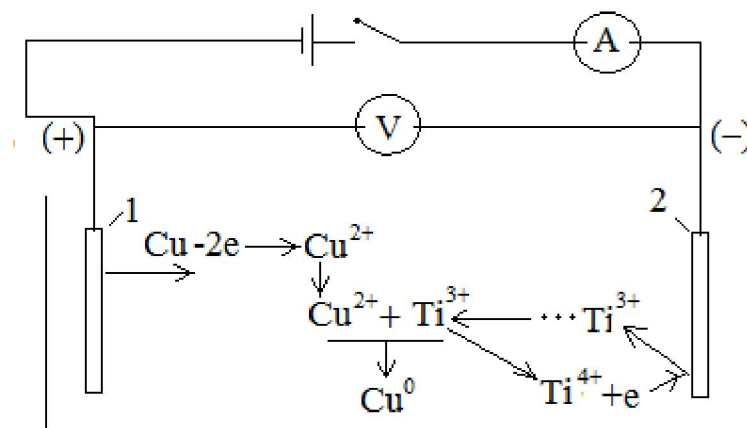


Figure 1 - Schematic diagram of the electrolyzer. 1 - copper electrode;
2 - titanium electrode; electrolyte composition: Ti(IV) + H₂SO₄

In the cathode, titanium (IV) ions are oxidized to the tri-valent state.:



Copper (II) and Ti (III) ions, formed during reactions (1) and (2), are found among the electrodes and, as a result, nano-scale copper powders are formed.



As it is shown in Figure 1, tetra-valent titanium ions formed as a result of reaction (3) in the cathode are again oxidized to the trivalent state during reaction (2), interacting with copper (II) ions between the electrodes and the formation of copper powders is again based on the reaction (3). These processes are cyclically repeated. The objective of the research is to study the effect of various parameters on the formation of copper powders by the mentioned mechanism..

Experimental. The formation of copper powders was investigated when exposed to a current density in the electrodes in the range of 50–1,200 A/m². Within the current density range in the electrodes, 50-150 A/m², the formation of copper powders is 100%. It should be noted that on the basis of reaction (3) a very dispersed colloidal copper is formed. Only after an hour they connect and increase, then precipitated. Increasing the current density in the electrodes reduces the current consumption of the formation of copper powders. This phenomenon can be explained by the course of an additional reaction in the electrodes at a high current density. At this time, copper powders are still formed on the surface of the cathode. In the cathode, in addition to the main oxidation reaction of titanium (IV) ions in the 2nd reaction, the oxidation reaction of other hydrogen ions also takes place:



As a result, the current consumption of titanium (IV) ion oxidation decreases and the formation of copper powders is reduced during the reaction (3).

It stands to mention that when electrolysis is carried out in a low current density of 100-150 A/m², without involving of titanium (IV) ions, ionization of copper electrodes is observed in the first reaction (1) and after some time oxidation of copper (II) ions on the cathode surface.



The distance between the anode and cathode electrodes is 4-6 cm or more, also in the presence of titanium (IV) ions in the solution, the oxidation of copper ions to copper powders is not carried out immediately, but after a certain time between the electrodes.

The impact of sulfuric acid on the formation of copper powders in the range of 50-250 g/L (Table 1) was investigated. There is a decrease in the current consumption for the formation of copper powders after the increase in acid concentration. This phenomenon can be explained by a slight dissolution of the formed dispersed powders in sulfuric acid. Since electrolysis is carried out in the open air, the following reaction can take place:



Table 1 - The impact of acid concentration on the current consumption of the formation of copper powders:

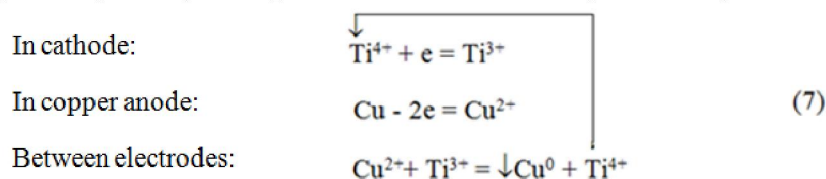
Ti(IV) = 8 g/L, $i = 150 \text{ A/m}^2$, $\tau = 30 \text{ minutes}$, $t = 25^\circ \text{C}$

| | | | | | |
|-------------------------------|-------|-------|-------|-------|------|
| H_2SO_4 , g/L | 50 | 100 | 150 | 200 | 250 |
| CO_2 , % | 109,2 | 110,0 | 111,1 | 104,5 | 95,3 |

The impact of the concentration of tetra-valent titanium ions on the formation of copper powders in the range of 1–16 g/L during electrolysis was studied. In the absence of titanium (IV) ions in the solution between the electrodes, the formation of copper powders is not observed. The results of the study showed that, depending on the increase in the concentration of titanium (IV) ions in solution, the current consumption of the formation of copper powders increases..

With an increase in the concentration of titanium (IV) ions in the solution, the current consumption of their oxidation to the tri-valent state in the cathode increases, and the rate of formation of copper powder increases according to reaction (3). As a result, we can say that the current consumption of the copper powders formation is growing..

When conducting electrolysis using copper and titanium electrodes in a solution of sulfuric acid with titanium (IV) ions, the following cyclic mechanism took place: copper (II) ions $\text{Cu} - 2e = \text{Cu}^{2+}$ are formed in the anode, at this time the electrolyte color in the anode area begins to acquire blue shade, in the cathode, tetra-valent titanium ions are oxidized to the tri-valent state and in this area of the electrode the color of the electrolyte turns purple. Further, these ions collide between the electrodes and as a result of reaction (3) dispersed copper powders are formed. At this time, the formed tetra-valent titanium ions are diffused towards the cathode and are oxidized again to the tri-valent state on the surface of the cathode. This reaction is repeated cyclically. This process can be shown as a general diagram as follows:



As can be seen from reaction (7), under the above conditions, the titanium (IV) - titanium (III) scheme acts as a catalyst system, these processes are repeated cyclically.

It should be noted that with a smaller distance between the anode and cathode, as well as a high current density in the electrodes, the dissolution current consumption of copper will be 100%, and the oxidation current consumption of titanium (IV) ions will decrease dramatically. In this case, an excess of copper (II) ions formed in the anode is oxidized forming copper powders under the conditions of a current density limited in the cathode. At this time, the formation of copper powders takes place both between the electrodes and on the surface of the cathode.

Microphotographs of copper powders obtained under various electrolysis conditions were taken and studies were carried out. An electron microscope of the JSM6610W model was used in these studies.

It is established that in the electrode area very dispersed sphere-shaped powders are formed. Figure 3 shows a microphotograph of copper powders formed between the electrodes at a current density 150 A/m^2 in the electrodes. The average size of copper particles $0.1\text{-}0.2 \text{ }\mu\text{m}$.

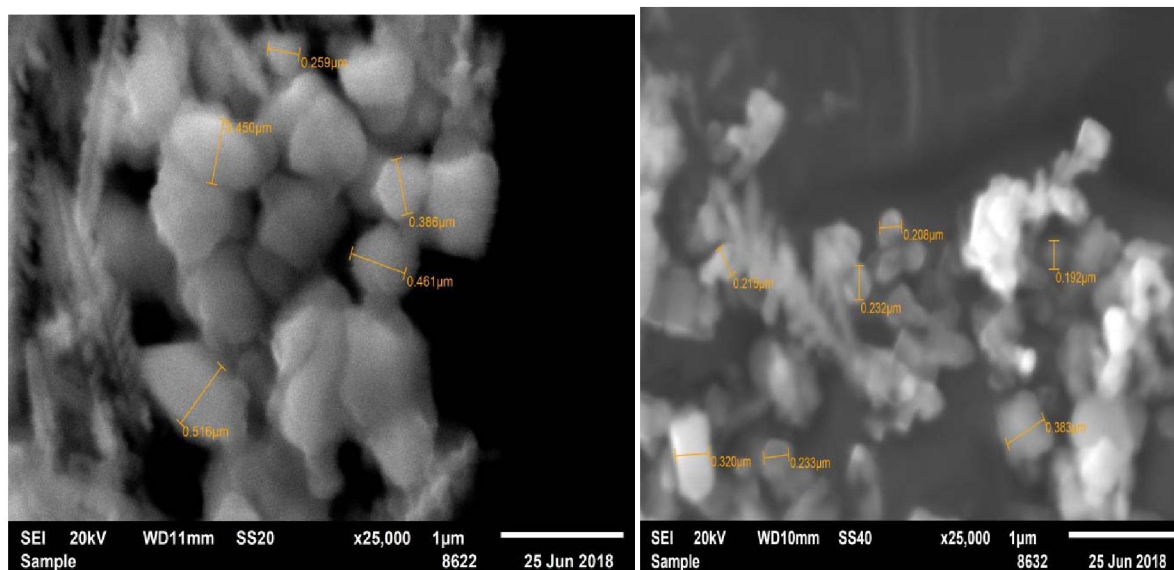


Figure 4 - Microphotograph of copper powders, formed between electrodes $i=150 \text{ A/m}^2$, $\text{Ti(IV)} = 8 \text{ g/L}$, $t = 25^\circ\text{C}$

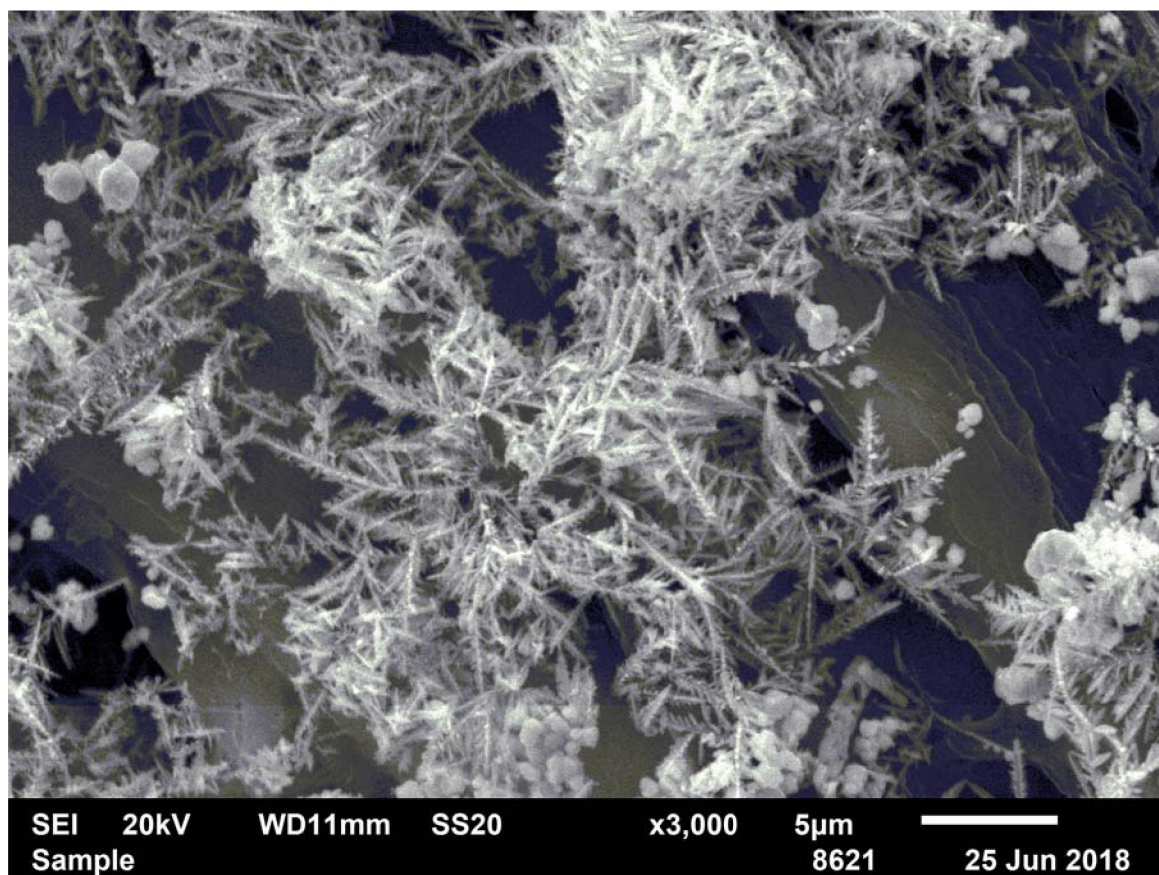


Figure 5 - Microphotograph of copper powders, formed on the surface of cathode $i=1200 \text{ A/m}^2$, $t = 25^\circ\text{C}$

Figure 5 shows microphotographs of copper powders formed on the surface of the cathode at a current density 1200 A/m^2 in the electrodes. In this case, it was found that copper powders in the form of threads are formed on the cathode surface.

In conclusion, for the first time when using the copper anode in a sulfuric acid solution with titanium (IV) ions, when using a copper anode between the electrodes under certain conditions, a very dispersed

copper powder is formed, the impact of various parameters on this process is investigated. It has been established that between the electrodes copper particles are formed in the sphere shape with an average size of 0.1-0.2.

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ҚҰРАМЫНДА ТИТАН (IV) ИОНДАРЫ БАР КҮКІРТ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕ МЫС АНОДЫН ҚОЛДАНУ КЕЗІНДЕ ЭЛЕКТРОЛИТ КӨЛЕМІНДЕ ДИСПЕРСТІ МЫС ҰНТАҚТАРЫНЫҢ ТҮЗІЛУ ЗАҢДЫЛЫҚТАРЫ

Аннотация. Құрамында титан (IV) иондары бар күкірт қышқылы ерітіндісінде “мыс-титан” жұбы электродын поляризациялау кезінде электродтар кеңістіктері аралығында дисперсті мыс ұнтақтарының түзілетіндігі алғаш рет көрсетілді.

Электролиз кезінде мыс ұнтақтарының түзілуі механизмі зерттелді. Мыс және титан электродтарын Ti(IV) иондары бар күкірт қышқылды ерітіндіге салып поляризацияланған кезде, мыс аноды мыс(II) иондарын түзе еріп, ал катодта титан (IV) иондары үш валентті күйге дейін тотықсызданатындығы көрсетілді. Бұл кезде катод аумағындағы электролиттің түсі – күлгін, ал анод аумағында – көк түске өтеді. Түзілген мыс (II) және Ti (III) иондары электродтар аралығында бір-бірімен кездесіп, нәтижесінде наноразмерлі мыс ұнтағы түзілетіндігі анықталды.

Реакция нәтижесінде түзілген төрт валентті титан иондары катодта қайтадан үш валентті күйге дейін тотықсызданып, ол электродтар аралығында мыс (II) иондарымен әрекеттесіп қайтадан мыс ұнтағының түзілетіндігі және бұл процестер циклілі түрде қайталанып тұратындығы көрсетілді. Электролиз кезінде электродтар аралығында алғашқыда коллоидты мыс ұнтақтарының түзілетіні және олардың бір-бірімен бірігіп содан кейін тұнбаға түсетіндігі көрсетілді.

Түйін сөздер: титан иондары, мыс, ұнтақ, электролиз, электролит, тотықсыздану

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**ЗАКОНОМЕРНОСТИ ОБРАЗОВАНИЯ ДИСПЕРСНЫХ МЕДНЫХ ПОРОШКОВ
В ОБЪЕМЕ ЭЛЕКТРОЛИТА ПРИ ИСПОЛЬЗОВАНИИ МЕДНОГО АНОДА
В РАСТВОРЕ СЕРНОЙ КИСЛОТЫ, СОДЕРЖАЩЕЙ ИОНЫ ТИТАНА (IV)**

Аннотация. Впервые показано, что при поляризации пары электродов «медь-титан» в растворе серной кислоты, содержащей ионы титана (IV) в межэлектродном пространстве образуются медные порошки.

Исследован механизм образования медных порошков при электролизе. Показано, что при поляризации электродов меди и титана в растворе серной кислоты, содержащей ионы титана (IV), аноды меди растворяются, образуя ионы меди (II), а на катоде ионы титана (IV) восстанавливаются до трехвалентного состояния. В это время цвет электролита на катоде – фиолетовый, а на аноде – переходит в синий цвет. Установлено, что образованные ионы меди (II) и Ti (III) взаимодействуют в объеме раствора между электродами, в результате образуются наноразмерные медные порошки.

Показано, что четырехвалентные ионы титана, образованные в результате реакции снова восстанавливаются на катоде до трехвалентного состояния в свою очередь в межэлектродном пространстве они снова взаимодействуют с ионами меди (II), образуя медные порошки и эти процессы циклично повторяются. Показано, что при электролизе между электродами сначала образуются коллоидные медные порошки, затем они соединяются и оседают.

Ключевые слова: ионы титана, медь, порошки, электролиз, электролит, восстановление.

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