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# Х А Б А Р Ш Ы С Ы

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**ВЕСТНИК**

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
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E-mail: bayeshov@mail.ru, diko77781@mail.ru, tvoyaulibka@mail.ru**STUDY OF ELECTROCHEMICAL PROPERTIES OF COPPER  
IN SOLUTION OF SULPHURIC ACID WITH COPPER (II) IONS  
AND TITAN THROUGH POTENTIODYNAMIC POLARIZED CURVE**

**Abstract.** The electrochemical properties of copper, titanium in sulfuric acid and their ions in aqueous solution are investigated in the potentiodynamic mode by the method of polarization curves. Electrochemical properties of copper and titanium electrodes in a solution of sulfuric acid involving copper (II) ions and titanium with variable valency by means of potentiodynamic polarization curves. The recovery of copper (II) ions and the regularity of dissolution of the electrodes are determined. The reduction wave of tetravalent titanium ions in a solution of sulfuric acid with copper and titanium electrodes is registered for the first time in the polarization program, and it is indicated that the reduction wave of trivalent titanium ions in the above electrodes is not registered. It is also determined that when copper (II) ions are present in the electrolyte composition, the reduction wave of tetravalent titanium ions in the polarization curve is not registered. It is known that obtaining the main part of copper powders is performed by electrochemical method [1-12].

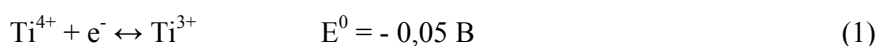
**Key words:** copper, titanium, electrodes, copper powders, sulfuric acid, electrolysis potentiodynamic curves.

Previous studies have shown that when titanium (IV) ions are present in the composition of the copper (II) solution with sulfuric acid, the formation of copper powders in the cathode increases in current and fine metal powders are formed [10, 13-16]. The study of the electrochemical properties of copper, titanium in a solution of sulfuric acid and their ions in an aqueous solution, in order to understand the mechanism of these processes is carried out in the Abtolab potentiostat in the potentiodynamic mode using the polarization curve method.

The main potentiodynamic polarization curves were captured at a 50 mV/s of potential change rate. The reference electrode is a silver-chloride electrode ( $E = + 0,203B$ ), and platinum or graphite electrodes are used as auxiliary electrodes. The values of the potentials was compared to the silver-chloride electrode. Before the tests, the electrodes were cleaned with emery-paper to remove the oxide film and then washed with alcohol, then with distilled water and wiped with paper filter. The thermostat and a special YaSE-2 electrochemical cell was used to conduct research at constant temperatures.

Literature data [16,17] and the results of our research show passivity of titanium electrode during anode polarization in solutions of sulfur and hydrochloric acids, and cathodic polarization curves show that only hydrogen is released.

Data on the oxidation-reduction reactions of titanium (IV) and titanium (III) ions in the acidic environment are insignificant in the literature because polarization curves do not show the oxidation and reduction waves before hydrogen and oxygen release potential of these ions. Some articles mention only the standard potential value of the reduction of the tetravalent titanium to trivalent ions [18-22]:



Thus, some of the titanium (IV) ions can be reduced by cementing with some negative potential metals. Such negative potential valued metals are - lead, zinc etc. There is also information in the literature that these ions are oxidized by hydrogen-contained, carbon-contained and some other metallo-organic

compounds. However, the reduction of titanium (IV) ions at room temperature is considered to be at low speeds. As per known methods, trivalent titanium ions are obtained by reduction of tetravalent titanium in cathode environment for several hours.

Typically, when obtaining copper powder the titanium electrode is used as a cathode, and in the sulfuric acid solution the cathode potentiodynamic polarization curve of this electrode shows only the hydrogen ions reducing current (figure 1). The results show that as the sulfuric acid concentration increases, cathodic potentiodynamic curves show a significant reduction in the hydrogen release current. This phenomenon is associated with the increase in the concentration of hydrogen ions.

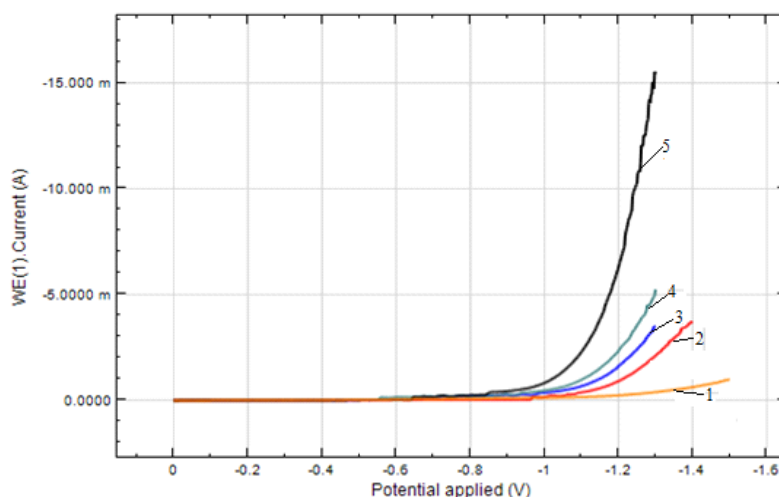


Figure 1 – The cathode polarization curves recorded in the titanium electrode of the sulfuric acid solution at  $V = 50 \text{ mV/s}$ ,  $t = 25 \text{ }^\circ\text{C}$ ,  $\text{H}_2\text{SO}_4 \text{ g/l}$ : 1 - 10, 2 - 25, 3 - 50, 4 - 75, 5 - 100

When adding copper (II) ions to the sulfuric acid solution, the polarogram captures its maximum reduction at the titanium cathode. With the increase in copper (II) ions, the increase in the maximum current values of reduction is observed (figure 2).

As the concentration of copper (II) ions in the solution grows, it is possible to notice that the hydrogen ions discharge voltage drops significantly. This phenomenon can be explained by the fact that in the copper electrode the hydrogen is released with less volatile than in titanium.

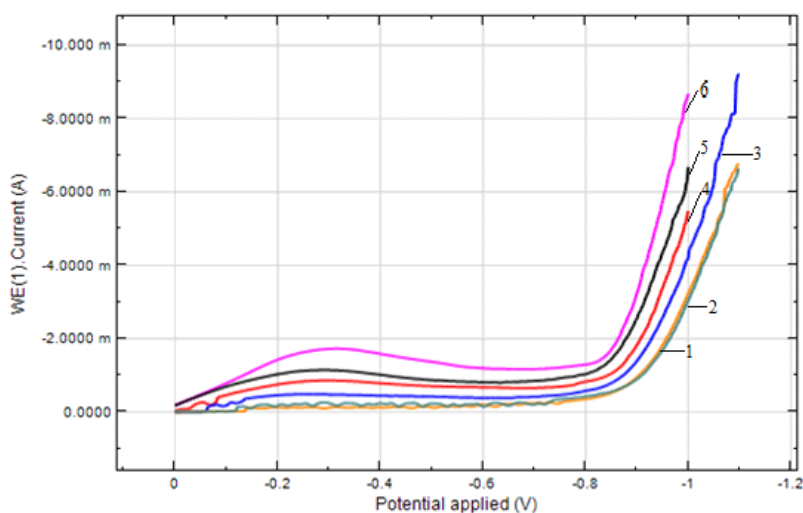


Figure 2 – Cathode polarization curves registered in titanium electrode at concentrations of various copper (II) ions in the sulfuric acid solution,  $V = 50 \text{ mV/s}$ ,  $t = 25 \text{ }^\circ\text{C}$ ,  $\text{H}_2\text{SO}_4 - 50 \text{ g/L}$ ,  $\text{Cu(II), g/L}$ : 1 - 1,0; 2 - 2,5; 3 - 5,0; 4 - 10; 5 - 15; 6 - 20

When adding tetravalent titanium ions to the copper (II) in sulfuric acid solution, the reduction current of the obtained ions are not observed in the polarogram. And in the pure sulfuric acid solution, the subtly visible reduction wave of the tetravalent titanium ions is recorded in the cathode potentiodynamic curve (figure 3).

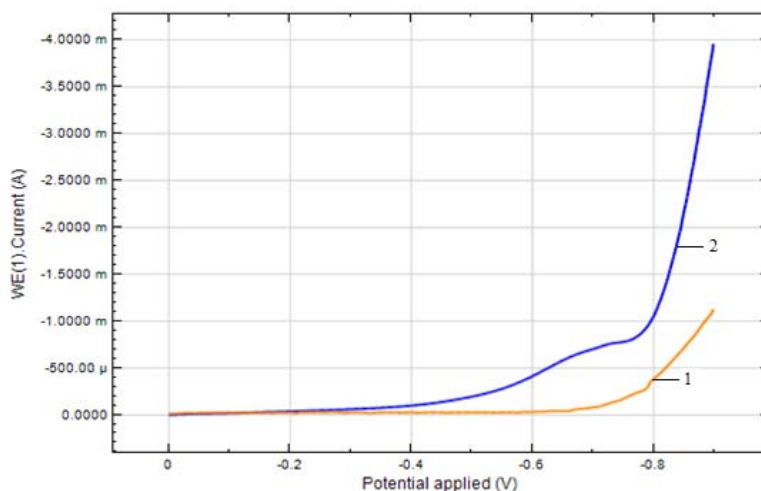


Figure 3 – Cathodic polarization curve recorded on a titanium electrode in a solution of sulfuric acid containing titanium (IV) ions (IV): 1 - 10 g/L  $H_2SO_4$ ; 2 - 10  $H_2SO_4$  g/L+ 10 g/L titanium (IV);  $V = 50$  mV/s;  $t = 25$  °C

In the process of electrolysis copper (II) ions are reduced in cathode, then after short time covering the titanium surface, functions as copper electrode. Therefore, in order to fully understand the mechanism of reactions occurring in the electrodes during the formation of copper powders, the following studies were conducted on the copper electrode.

The cathode polarization curves recorded in the copper electrode in the sulfuric acid solution show a decrease in the voltage of the reduction of hydrogen ions due to the increase in electrolyte acidity (figure 4).

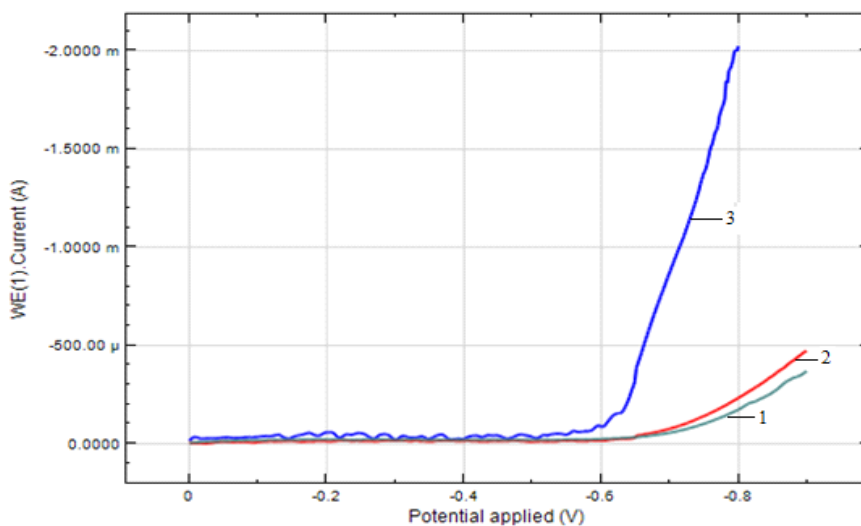


Figure 4 – Cathode polarization curves recorded from copper electrode in sulfuric acid solution,  $V = 50$  mV/s;  $t = 25$  °C;  $H_2SO_4$ , g/L: 1 - 50; 2 - 75; 3 - 100

When adding copper (II) ions to the sulfuric acid solution, the cathode reduction maximum rate in the polarogram is recorded and the maximum value increases with straight linearity regularity due to the increase in concentration of copper (II) ions (figure 5).



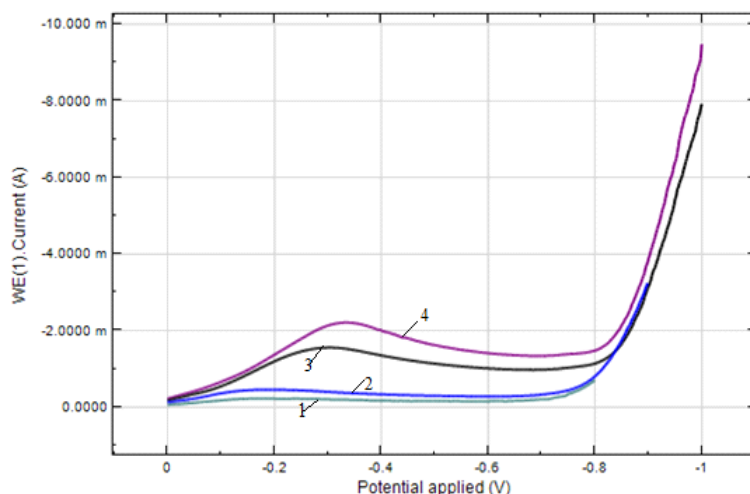


Figure 5 – Cathode polarization curves of copper electrode in sulfuric acid solutions with different concentrations of copper (II) ions,  $V = 50 \text{ mV/s}$ ,  $\text{H}_2\text{SO}_4 - 50 \text{ g/L}$ ,  $\text{CuSO}_4$ , g/L: 1 - 5,0; 2 - 10; 3 - 15; 4 - 20

In the above case, the increase in the rate of potential transfer increases the maximum of copper (II) ions reduction (figure 6). It is assumed that the reduction of copper (II) ions occurs in the diffusion mode.

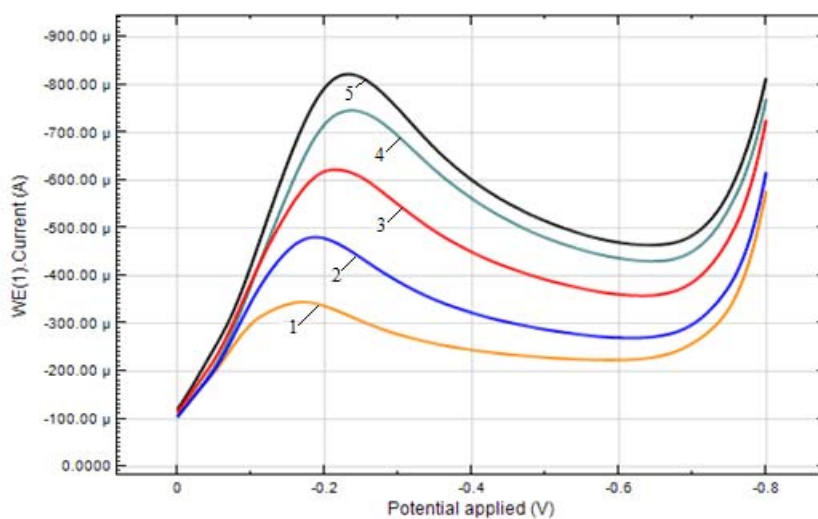


Figure 6 – Cathode polarization curves of copper electrodes in sulfuric acid solution with copper (II) ions,  $50 \text{ g/L H}_2\text{SO}_4 + 10 \text{ g/L CuSO}_4$ ,  $V = 50 \text{ mV/s}$ : 1 - 25; 2 - 50; 3 - 100; 4 - 150; 5 - 200

When adding titanium (IV) ions to sulfuric acid solution with copper (II), the reduction wave of subsequent ions in the copper electrode is not observed in the polarogram. In the pure sulfuric acid solution, the reduction wave of the tetra-valent titanium ions is clearly marked on the polarogram (figure 7).

Copper electrodes are used as copper anodes when copper powders are obtained from the sulfuric acid copper (II) solution. Therefore, electrochemical properties of copper electrode in sulfuric acid solution with copper (II) ions were investigated.

Anode, cathode and cyclic polarization curves were recorded for the copper electrode in the sulfuric acid solution. When polarization begins to grow in the direction of the anode, the maximum current in the polarogram is registered. On the surface of the electrode copper oxide is formed, passivated and the value of the current decreases dramatically. Copper potential is further reduced to the right when copper melting occurs at a very low speed under transpassivation (figure 8), and increase in the rate of the potential transfer of copper the copper dissipation maximum rate increases (figure 9).

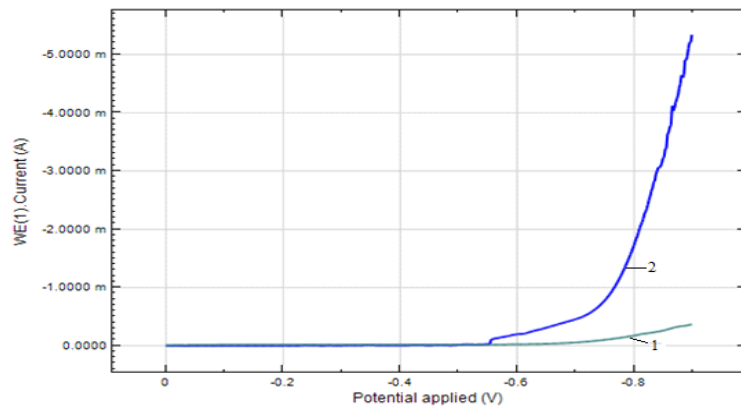


Figure 7 – Cathode polarization curves recorded for copper electrode in sulfuric acid solution with titanium (IV) ions:  $H_2SO_4 - 20g/L$ ; titanium (IV) – 30 g/L

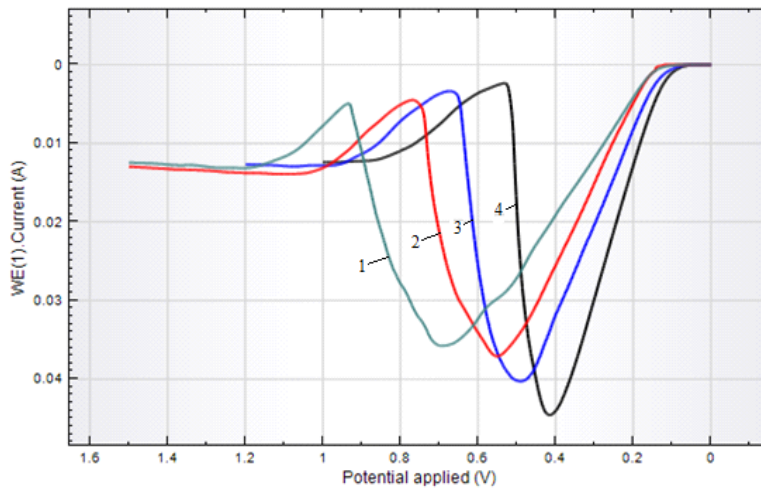


Figure 8 – Anode polarization curves of various copper electrodes in sulfuric acid solutions:  $V = 50\text{ mV/s}$ ;  $t = 25\text{ }^\circ\text{C}$ ;  $H_2SO_4$ , g/L: 1 - 50; 2 - 75; 3 - 100; 4 - 150

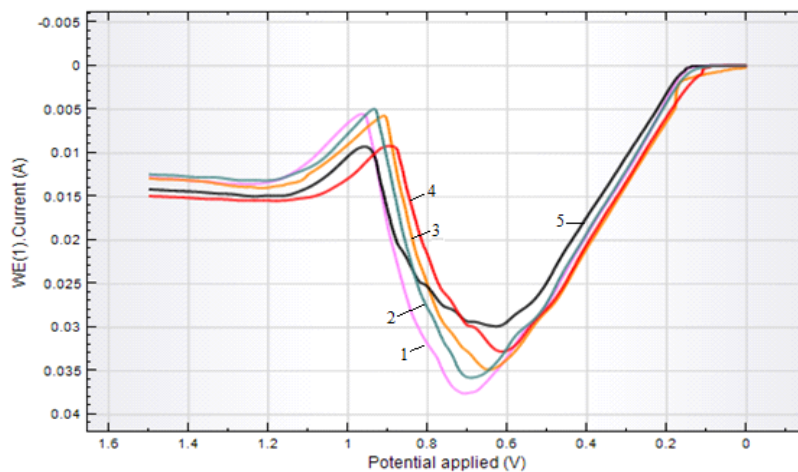


Figure 9 – Copper electrode polarization curves in sulfuric acid solution with different concentrations of the copper (II) ions,  $H_2SO_4 - 50\text{ g/L}$ ,  $V = 50\text{ mV/s}$ ,  $CuSO_4$ , g/L: 1 - 1,0; 2 - 2,5; 3 - 5,0; 4 - 7,5; 5 - 10,0

The presence of copper ions in the sulfuric acid solution and its concentration increase slightly increase the maximum anode value.

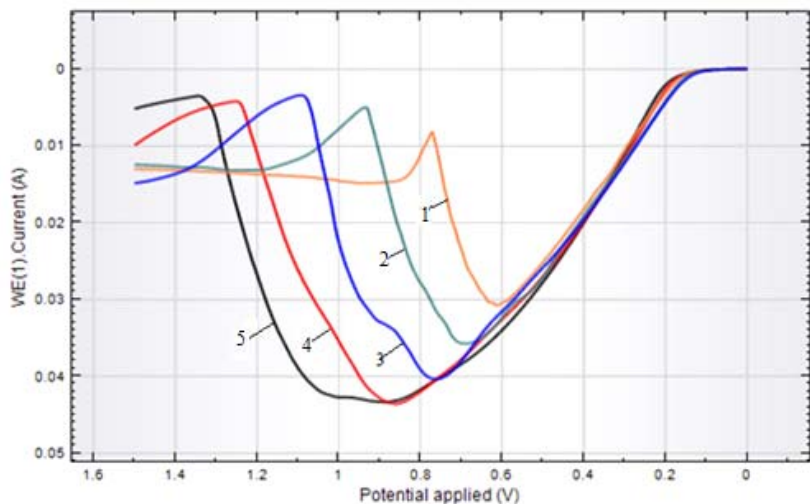


Figure 10 – Anode polarization curves of different potential transfer rates of the copper electrode in the sulfuric acid solution,  $H_2SO_4$  - 50 g/L,  $V$ , mV/s: 1 - 20; 2 - 50; 3 - 100; 4 - 150; 5 - 200

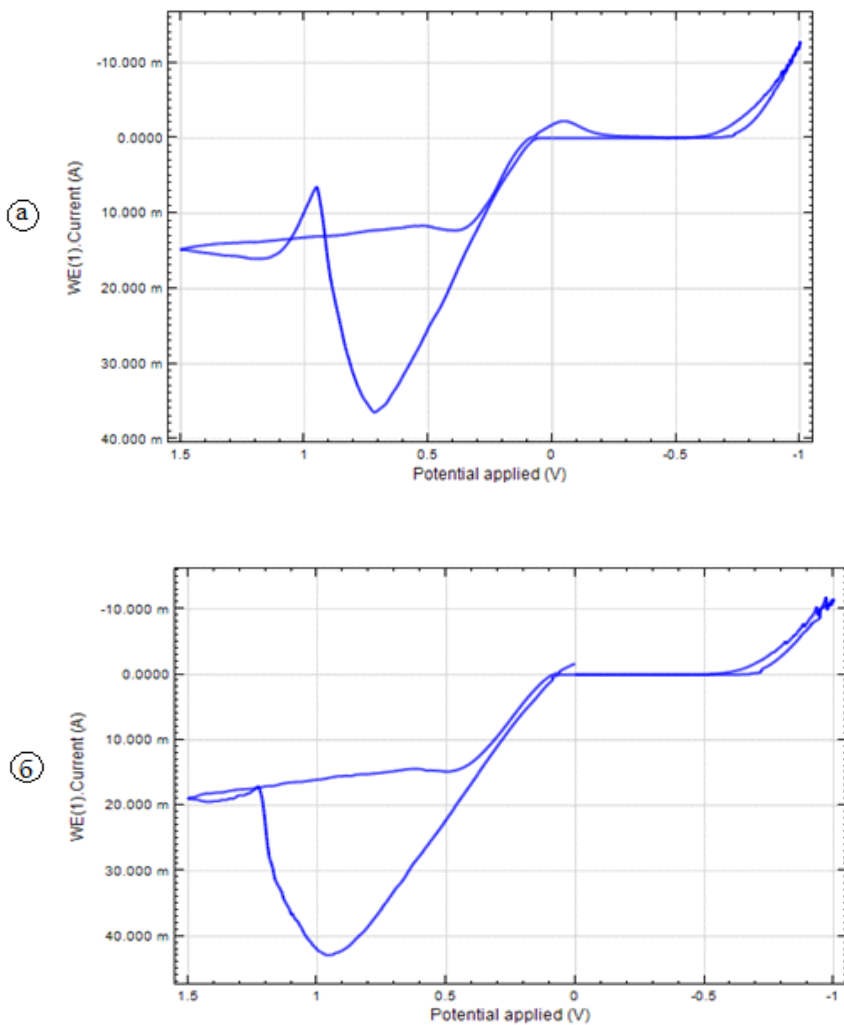


Figure 11 – Potential anodic-cathode (a) and cathodic-anode (b) potentiodynamic polarization curves of copper electrode in the 50 g/L sulfuric acid solution,  $V = 50$  mV/s;  $t = 25$  °C

Electrochemical properties of copper electrode in sulfuric acid solution were also studied by cyclic potentiodynamic curves.

When the copper electrode in the sulfuric acid solution is displaced to the potential anode direction, as it was shown previously, it is melting, followed by an oxidizing film forming, which is then passivated, and then starting from the 10.0V potential area continues to melt at low velocities under transpassivation. Oxygen gas release is not observed (up to "plus" 1.5 V). And when the potential is displaced to negative potentials, the maximum reduction rate of the copper oxide film formed on the surface of the electrode within the area of 0.0V potentials is registered, and at the "minus" 0.7V potential the hydrogen ion discharge current is registered on the polarogram (figure 11a).

And in the cathodic-anode cyclic polarogram, the above reactions take place (figure 11b).

We cannot see the oxidation current of the tri-valent titanium ions on titanium and copper electrodes in anode polarization curves.

Summarizing the above, the electrochemical properties of copper and titanium electrodes in the sulfuric acid solution in relation with copper (II) and mixed-valence titanium ions were investigated by potentiodynamic polarization curves. The regularities of copper (II) ions reductions and copper electrodes melting are determined. The reduction wave of copper and titanium electrodes of the tetravalent titanium ions in the sulfuric acid solution were recorded for the first time on the polarogram, and the oxidation waves of the trivalent titanium ions were not recorded in the above electrodes. We found that when the electrolyte contains copper (II) ions the reduction wave of tetravalent titanium ions was not registered in polarization curves.

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#### **МЫС (II) ЖӘНЕ ТИТАН ИОНДАРЫ БАР КҮКІРТ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕ МЫСТЫҢ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІН ПОТЕНЦИОДИНАМИКАЛЫҚ ПОЛЯРИЗАЦИЯЛЫҚ ҚИСЫҚТАР ТҮСІРУ АРҚЫЛЫ ЗЕРТТЕУ**

**Аннотация.** Күкірт қышқылы ерітіндісінде мыстың, титанның және олардың иондарының сулы ерітінділеріндегі электрохимиялық қасиеті потенциодинамикалық режимде, поляризациялық қисықтар түсіру әдісімен зерттелінді. Мыс және титан электродтарының күкірт қышқылы ерітіндісінде, мыс (II) және айнымалы валентті титан иондары қатысында электрохимиялық қасиеттері потенциодинамикалық поляризациялық қисықтар түсіру арқылы зерттелді. Мыс (II) иондарының тотықсыздануы және мыс электродының еру заңдылықтары анықталды. Төрт валентті титан иондарының күкірт қышқылы ерітіндісінде мыс және титан электродтарында тотықсыздану толқыны алғаш рет полярограммада тіркелді, ал үш валентті титан иондарының тотығу толқындарының жоғарыда көрсетілген электродтарда тіркелмейтіндігі көрсетілді. Электролит құрамында мыс (II) иондары бар кезде төрт валентті титан иондарының тотықсыздану толқынының поляризациялық қисықтарда тіркелмейтіндігі анықталды. Мыс ұнтақтарының негізгі бөлігі электрохимиялық тәсілдермен алынатындығы белгілі [1-12].

**Түйін сөздер:** мыс, титан, электродтар, мыс ұнтақтары, күкірт қышқылы, электролиз, потенциодинамикалық қисықтар.

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#### **ИССЛЕДОВАНИЕ ЭЛЕКТРОХИМИЧЕСКОГО ПОВЕДЕНИЯ МЕДИ В РАСТВОРЕ СЕРНОЙ КИСЛОТЫ, СОДЕРЖАЩИХ ИОНЫ МЕДИ (II) И ТИТАНА МЕТОДОМ СНЯТИЯ ПОТЕНЦИОДИНАМИЧЕСКИХ ПОЛЯРИЗАЦИОННЫХ КРИВЫХ**

**Аннотация.** Электрохимические свойства меди, титана в серной кислоте и их ионов в водном растворе исследуется в потенциодинамическом режиме методом поляризационных кривых. Электрохимические свойства электродов меди и титана в растворе серной кислоты с участием ионов меди (II) и титана с переменной

валентностью путем потенциодинамических поляризационных кривых. Определяется восстановление ионов меди (II) и закономерность растворения электродов. Волна восстановления ионов четырехвалентного титана в растворе серной кислоты электродами меди и титана зарегистрирована в первый раз в поляропрограмме, а указывается, что волна восстановления ионов трёхвалентного титана в вышеуказанных электродах не зарегистрирована. Также определяется, что при наличии в составе электролита ионов меди (II) волна восстановления ионов четырехвалентного титана в поляризационной кривой не зарегистрирована. Известно, что получение основной части порошков меди производится электрохимическим способом [1-12].

**Ключевые слова:** медь, титан, электроды, медные порошки, серная кислота, электролиз, потенциодинамические кривые.

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