

Mechanisms for Ultrafine Copper Powders Electrolytes Production in the Presence of Titanium Ions

Abduali Bayeshov¹, Azhar Bayeshova^{2*},
Umida Abduvaliyeva³ and Aksulu Buketova⁴

¹Kazakh-Russian International University, Aktobe, Republic of Kazakhstan

²Center of Physical Chemical Methods of Research and Analysis and Department of General and Inorganic Chemistry, Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan

³Institute of Fuel, D.V. Sokolskiy's Catalysis and Electrochemistry, Almaty, Republic of Kazakhstan

⁴Kazakh British Technical University, Almaty, Republic of Kazakhstan

*Corresponding author: azhar_b@bk.ru

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Abstract

Copper (Cu) powder production, in a sulfuric acid (H₂SO₄) solution with titanium (Ti) ions, was studied by electrolysis, using Cu anodes. It was empirically proven that this process occurs by three different stage-based mechanisms that depend on the electrolyte composition and electrolysis conditions. The first mechanism occurs in a H₂SO₄ solution with Cu²⁺ ions and Ti⁴⁺ (tetravalent ions). Cu²⁺ are cathodically reduced, forming Cu powder (CP), since the process occurs at current densities (J) lower than the limiting one. So, part of the current that would be consumed by the hydrogen ions (H⁺) reduction reaction is spent to reduce Ti⁴⁺, which results in Ti³⁺ (trivalent ions). These, in the cathode space, reduce Cu²⁺, which, simultaneously, regenerates Ti⁴⁺. Then, these diffuse and are again reduced at the cathode, and Ti³⁺ are formed, reducing Cu²⁺, in a cyclic process that further increases CP production current efficiency (CE) at the near-cathode space, forming more dispersed particles. The second mechanism occurs in a H₂SO₄ solution with only Ti⁴⁺. During the electrochemical circuit current flow, the Cu anode is oxidized to form Cu²⁺, and Ti⁴⁺ are reduced to Ti³⁺, on the cathode surface. Then, Cu²⁺ and Ti³⁺, by diffusing the solution volume and meeting in the inter-electrode space, chemically interact with each other, due to the red-ox (reduction-oxidation) potential difference, forming a dispersed CP and Ti⁴⁺. These diffuse one more time, and are again reduced to Ti³⁺. These processes are cyclically repeated, i.e., Ti⁴⁺ work as catalyst. The third mechanism takes place in H₂SO₄ with Ti³⁺. When the current flows through the electrolyte, the Cu anode is oxidized, forming Cu²⁺, which are immediately reduced in the anode by Ti³⁺, producing CP. Ti⁴⁺ are formed due to the red-ox reaction diffusion to the cathode, being reduced to Ti³⁺ on its surface, which again interact with Cu, producing CP on the anode. Since, in all mechanisms (except the first), CP is not directly produced on the cathode surface, but in the inter-electrode space, further growth of Cu particles does not occur. Thus, CP particles of spherical shape, with sizes from 0.01 to 0.1 μm, are formed, with a CE from 95.2 to 99.1%, under optimal conditions.

Keywords: ultrafine CP production mechanisms, H₂SO₄ solution and Ti⁺ electrolytes.

Introduction

Metal powders and their production, especially ultrafine dispersed particles, are highly regarded as essential materials for different industries, such as nanotechnology, metallurgy, nuclear energy, space and mechanical engineering. Ultrafine CP is used in the chemical industry, and for powder metallurgy, because of its dispersity. Ultrafine dispersed CP is added to lubricant oils, for improving the wear resistance effect. It is also used to produce antifriction materials with metal and polymer matrix composites. CP can be used for the production of porous and permeable membranes, in chemical and engineering industries, and also as a catalyst in various oxidation reactions [1-7]. In addition, ultrafine CP has bactericide properties [8], and there is currently a focus on it, due to its dispersity. There are a variety of methods to obtain CPs with the desired characteristics. Electrolysis is the most widely used method, but has significant drawbacks, such as, when dissolved metal anodes are used, a noticeable imbalance between the anodic and cathodic reactions CEs occurs, whereby the former exceed 100%, while the latter are much lower. Accordingly, a constant accumulation of metal ions occurs in the electrolyte volume.

Traditionally, CP is produced by the electrolysis of salts aqueous solutions, at a current density (J) around 2000 A/m^2 , with a Cu low concentration in the electrolyte (10-13 g/L). Under these conditions, ions discharge rate onto the cathode is much higher than the rate of Cu ions transportation to the near-cathode space. In this case, the formation of a closed packed precipitate becomes impossible, and reduced Cu is precipitated in the form of powder.

The research of many scientists is devoted to the processes of obtaining CP by electrolysis, mainly focusing on the nature of Cu reduction at the cathode, under various electrolysis conditions. The influence of J , electrolyte temperature and various additives, has been established. The researchers explain the mechanism of formation of finely dispersed CP, and identify the conditions that increase its CE. This method effectiveness is very high, allowing the metal refinement with waste. It can be managed by changing the electrolysis schemes. However, non-oxidized metal powders with sufficiently high dispersion and electrical conductivity are not always obtained.

These powders can be produced, due to the sharp decrease in the discharged ions concentration at the near-cathode space, with J values above the limiting one. Under such conditions, a rapid and uneven growth of the cathode deposit is observed, with the accumulation of disparate small crystals aggregates, and the formation of a metal powder with different dispersion particles.

However, if J at the cathode is at its limit, almost all of the discharged ions disappear. In this case, even a small increase in J results in a significant potential shift to the negative side, which facilitates the H ions discharge. The corresponding chemical reactions at the cathode are described as follows:



where Me^n is a metal ion that can be reduced at the cathode under certain conditions (for example: Cu^{2+} , Cu^+ , etc.), n^+ is the ion charge or the metal oxidation degree, (for example, $^{2+}$, $^{3+}$, $^{4+}$, etc.), ne^{-} is the number of electrons that a metal ion accepts,

during the reduction at the cathode, under certain conditions, and Me^0 is a metal in its reduced form (for example, Cu^0).



where H^+ is a hydrogen ion, 2e^- is the number of electrons that it accepts during the reduction to its elemental state, and H_2 is a hydrogen molecule that was formed during the H^+ reduction.

The occurrence of a H evolution reaction (HER) naturally reduces the CE below 100%. In actual practice, J is reduced to 70-80%, which indicates that approxim. 20-30% of the current is lost by HER [9-13].

Based on the above-mentioned investigations, many opportunities exist today to improve existing methods and develop new approaches to CP production.

The aim of our work is to develop new electrochemical methods for obtaining dispersed CP in H_2SO_4 aqueous solutions with Ti^+ , and to elucidate the mechanism of powder formation, under various electrolysis conditions.

Experimental details

Material and methods

A Matrix MPS-305 D rectifying device was used as the current source. The current was measured by an E538 laboratory ammeter, and thermostating control was provided by a TW-2.02 thermostat. The CP size and form were identified by a JEOL JSM-6610LV electron microscope.

Sample preparation

The electrolysis was conducted in a 150 mL electrochemical cell, at 25 °C, and the following reagents were used: a H_2SO_4 aqueous solution; Ti^{3+} and Ti^{4+} (in the form of corresponding sulphates); Cu^{2+} (in the form of chemically pure Cu(II) sulfate pentahydrate: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$); Cu (99.99%) as anode; and Ti (99.70%) as cathode. Before starting the experiments, the electrodes were cleaned by abrasives, and carefully washed by distilled water. Then, they were dried using filter paper and alcohol. The CP obtained from the experiment was washed with water, stabilized using a 0,05% solution of Na soap, to prevent oxidation, dried and weighed. Three electrolysis types with different composites were studied: 10 g/L Cu^{2+} , 0-5.0 g/L Ti^{4+} and 100 g/L H_2SO_4 , at J from 1000 to 3000 A/m^2 , for 60 min; 50-200 g/L Ti^{4+} and 1-10 g/L H_2SO_4 , at J from 50 to 300 A/m^2 , for 30 min; and 50-150 g/L Ti^{4+} , 4.0 g/L Ti^{3+} and 10-20 g/L H_2SO_4 , at J from 150 to 350 A/m^2 , for 30 min, at 25 °C.

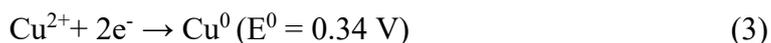
Results and discussion

Three new electrochemical mechanisms for producing CP, in the presence of Ti^+ , were investigated in this study. According to them, Cu reduction and further CP formation occurs in different ways, under diverse electrolysis conditions or electrolytes compositions.

CP production at the near-cathode space (mechanism 1)

During the Cu^{2+} and Ti^{4+} solution electrolysis, the following reactions take place on the Ti cathode:

a) Cu^{2+} reduction to Cu^0 , formed as a powder.



where Cu^{2+} is a Cu ion, in the oxidation state of 2^+ , $2e^-$ is the gain of 2 electrons of Cu^{2+} during Cu^{2+} reduction, Cu^0 is the elemental Cu obtained by Cu^{2+} reduction and E^0 is the standard potential of the Cu^{2+} reduction reaction; the value (0.34 V) was taken from the reference book.

b) at the same time, Ti^{4+} reduction to Ti^{3+} :



Both Ti^{4+} and Cu^{2+} were reduced on the cathode surface. In this case, the formed Ti^{3+} were the reducing agents. The generated Ti^{3+} reacted with Cu^{2+} at the near-cathode space, according to the reaction:



Cu^{2+} were furthermore reduced and Ti^{3+} were oxidized. Due to reaction (5), Ti^{4+} formation on the cathode and CP production near the cathode were observed.

$$\Delta E = E^0(\text{Cu}^{2+}/\text{Cu}^0) - E^0(\text{Ti}^{3+}/2\text{Ti}^{4+}) = 0.34 - (-0.04) = 0.38 \text{ V} \quad (6)$$

Equation (6) shows that the redox potential difference (ΔE^0) ($\text{Cu}^{2+}/\text{Cu}^0$ systems and $\text{Ti}^{3+}/\text{Ti}^{4+}$ systems) has a positive value (+0.38 V), which indicates that Ti^{3+} can reduce Cu^{2+} to Cu^0 state by reaction (5).

The possibility of the reaction (5) is also indicated by the equilibrium constant (K_{equil}) value equal to 10^{13} . Thus, Cu^0 powder is formed by reaction (5). As a result of this reaction, Ti^{4+} are formed, which are again reduced at the cathode by reaction (4). Ti^{3+} are again formed, which one more time reduce Cu^{2+} to Cu^0 and produce Ti^{4+} (5). All this shows that Ti^{3+} cyclically participate in Cu^{2+} reduction reaction, and are constantly regenerated.

Reaction (5) results in the production of an additional amount of CP. During the electrolysis, HER takes place, according to reaction (2).

It is important to note that reaction (2) is possible in the presence of Ti^{3+} , but the HER amount is not significant. Part of the current, which must be consumed in HER, is spent on Ti^{4+} reduction by reaction (4). As a result, an increase in the CE of Cu^0 powder production is observed, the magnitude of which is significantly affected by the Ti^{4+} concentration (Table 1).

Table 1. Influence of Ti^{4+} concentration on the electrolysis CE*.

Ti^{4+} (g/L)	0	1.0	2.0	3.0	4.0	5.0
CE%	71.8	84.3	89.1	93.7	95.2	95.2

*electrolyte: Cu^{2+} (8 g/L), H_2SO_4 (100g/L), J (2000 A/m²) and t (60 min).

Thus, there is CP production both on the cathode surface (reaction (3)) and at the near-cathode space (reaction (5)). The increase in CE (Table 1) results from reaction (5). As reaction (5) occurs at the near-cathode space, not on the cathode surface, the further growth of particles does not take place, and the process results in the production of ultrafine dispersed CP.

The schematic diagram of CP production (Fig. 1), according to the mechanism 1, can be explained as follows.

At the cathode, the reaction (3) proceeds, whereby Cu^{2+} are reduced to Cu^0 powder. The reaction (4) reduces Ti^{4+} to Ti^{3+} . According to the reaction (5), the formed Ti^{3+} are reducing agents, so, they interact with Cu^{2+} , and an additional amount of CP is formed. In this reaction, Ti^{4+} are simultaneously regenerated. Then, they diffuse and are again reduced at the cathode, and Ti^{3+} are formed. Ti^{3+} react again with Cu^{2+} and reduce them. This process is cyclically repeated. Thus, Ti^{4+} act as a catalyst. The course of these reactions is shown in Fig. 3, in the form of a diagram.

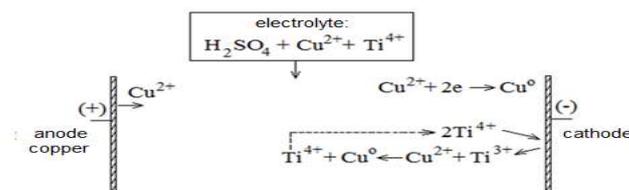


Figure 1. Scheme of Cu^{2+} reduction on the cathode surface, in the presence of Ti^{4+} .

CP obtained by the mechanism 1 was studied by electron microscopy. Microscopic images (Fig. 2 (a, b)) show that ultrafine CP, with an average particle size in the range from 0.1 to 3.0 μm , was produced. In Ti^{4+} absence, the electrolyte particle size ranged from 10 to 80 μm (Fig. 2 (c, d)).

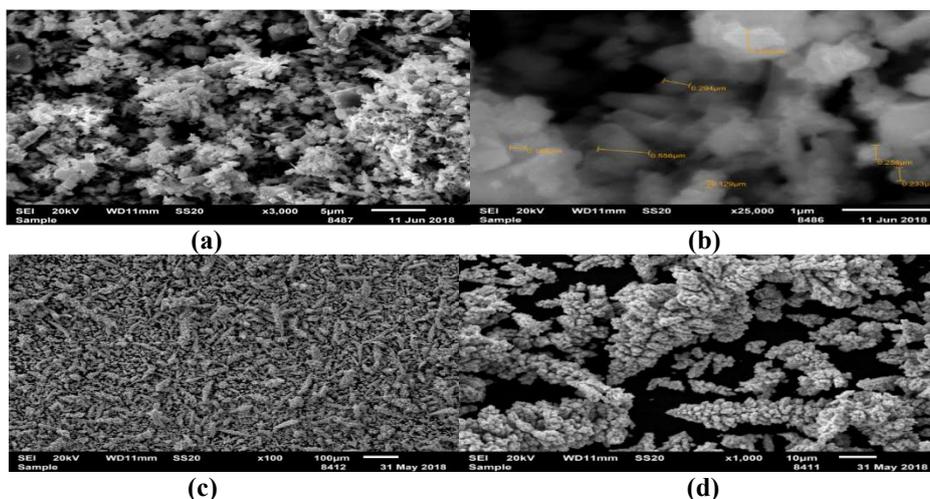


Figure 2. Microscopic photos of cathodic CP obtained (a, b) in the presence and (c, d) absence of Ti^{4+} . (a) magnification of 3000x, (b) magnification of 25000x, (c) magnification of 100x, (d) magnification of 1000x.

The experiment results allow us to infer that the current, which is completely spent on HER, in the traditional method, reduced Ti^{4+} and increased CP production, with Ti^{4+} regeneration. Thus, CP CE is significantly increased, and the particles size is decreased over 100 times.

CP production at the space between electrodes (mechanism 2)

The second type of electrolysis was performed in a H_2SO_4 solution containing Ti^{4+} without Cu^{2+} . Mechanism 2 is as follows: reactions (3, 5) take place as in the first

mechanism; the Cu anode dissolution forms Cu^{2+} ; Ti^{4+} are reduced to Ti^{3+} , at the cathode (reaction (4)); and the inter-electrode space chemical interaction generated between Cu^{2+} and Ti^{3+} produces Cu^0 powder, according to reaction (5).

This means that Ti^{3+} reduce Cu^{2+} . It should be noted that, at first, ultrafine Cu particles were produced in the form of a colloid. Then, after 30-60 min, Cu particles were precipitated in the form of powder.

Ti^{4+} are reduced to Ti^{3+} , according to reaction (4), and then regenerated, according to reaction (5). Hence, these reactions (4, 5) are cyclically repeated. It can be observed that Ti^{4+} are not consumed during the electrolysis, acting as a catalyst for Cu^{2+} reduction. According to reaction (5), CP is produced at the inter-electrode space.

The particles aggregation does not occur, because there is no possibility of Cu^{2+} direct reduction at the cathode surface.

The influence of Ti^{4+} , H_2SO_4 concentration and J, on CE, was investigated during the experiments. An increase in Ti^{4+} concentration, in the range from 1 to 10 g/L, results in an increase in CP CE, similar to mechanism 1. The highest CE value was close to 100%, obtained at J, from 50 to 150 A/m^2 (Table 2).

Table 2. J influence on CP CE*.

J (A/m^2)	50	100	150	200	250	300
CE%	99.05	99.10	99.18	89.3	87.2	82.5

*electrolyte: Ti^{4+} (10 g/L), H_2SO_4 (100 g/L) and t (30 min).

Table 3 shows that, in favourable conditions, with H_2SO_4 concentrations varying from 50 to 200 g/L, CE was in the range from 98.9 to 99.2%. These obtained values once again prove that the current was almost completely consumed by CP production, and that H was not released during the electrolysis.

Table 3. H_2SO_4 concentration influence on CP CE*.

H_2SO_4 (g/L)	50	100	150	200
CE%	98.9	99.1	99.8	99.2

*electrolyte: Ti^{4+} (10 g/L), J (100 A/m^2) and t (30 min).

The scheme of mechanism 2 for ultrafine CP production is shown in Fig. 3.

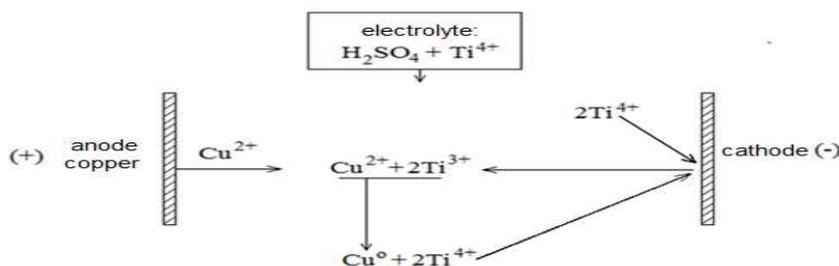


Figure 3. Schematic of CP production at the inter-electrode space.

Microscopic images of CP obtained in the inter-electrode space are shown in Fig. 4 (a, b). The average size of the spherical particles varies from 0.2 to 1.2 μm , and it becomes noticeable at a magnification of 25,000 times (Fig. 4(b)).

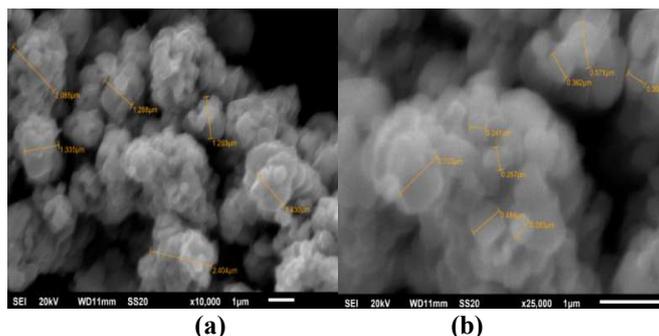


Figure 4. Images of CP obtained at the inter-electrode space, according to the scheme shown in Fig. 3: (a) 10,000 times magnification; (b) 25,000 times magnification.

CP production at the near-anode space (mechanism 3)

Electrolysis was conducted in a H₂SO₄ solution, containing Ti³⁺ and Ti⁴⁺. The third mechanism is as follows: the Cu anode was dissolved forming Cu²⁺; Ti³⁺ in the solution reacted immediately with the formed Cu²⁺ (according to reaction (5)); Cu⁰ resulted, at first, in a colloid form and, later, in powder; Ti³⁺ were oxidized to Ti⁴⁺; Ti⁴⁺ diffused to the cathode surface where they were reduced to Ti³⁺; and Ti³⁺ were diffused towards the near-anode space. At the anode surface, reaction (5) occurred again to produce dispersed CP, and all of the above processes were cyclically repeated. Ti⁴⁺ were reduced at the near-cathode space, through reaction (5), where Ti³⁺ reacted with Cu²⁺. The scheme of mechanism 3 is shown in Fig. 5.

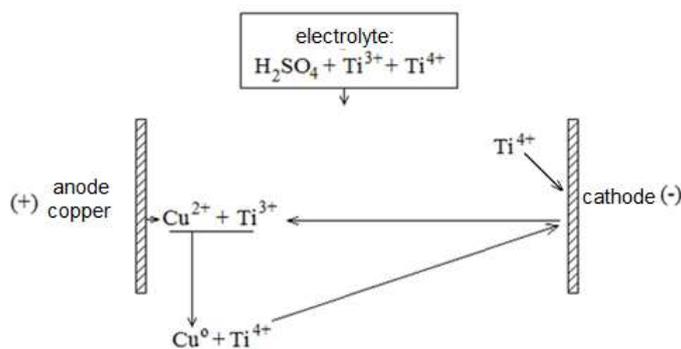


Figure 5. Schematic of CP production at the near-anode space.

As it can be seen from Table 4, any change in J and Ti⁴⁺ concentration, in the range from 150 to 350 A/m² and from 10 to 20 g/L, respectively, did not significantly affect the CE. An average CE of 99.62% was demonstrated under experimental conditions. This indicates that the current was almost completely spent by CP production. HER was not observed here. The microscopic images of obtained CP were very close to those produced by the second mechanism. The average size of CP particles was in the range from 0.01 to 0.1 μm.

Table 4. Influence of J and Ti⁴⁺ concentration on CP production CE *.

J (A/m²)	150	175	250	300	350
Ti⁴⁺ concentration, g/L	10	12	15	18	20
CE%	99.9	99.2	99.8	99.5	99.7

*electrolyte: H₂SO₄ (100 g/L) and t (30 min).

The experiments results show that Cu particles obtained by three different methods did not have the ability to grow during powder production, since the process did not occur directly at the cathode surface. In this case, the particles with only very small sizes were capable of growing, which resulted in a unification to ultrafine nanostructured forms. It is expected that CP with almost nano-sized particles is formed by mechanisms 2 and 3.

Conclusions

The research results have shown that, depending on the electrolyte compositions and electrolysis conditions, CP production can proceed by three different mechanisms.

- The main difference between the three powder production mechanisms was that it was formed in diverse parts of the electrolyte. CP can be obtained at the cathode and at the near-cathode space (mechanism 1), at the inter-electrode space, i.e. between the electrodes (mechanism 2), and at the near-anode space (mechanism 3).
- In all three cases, the powder production process proceeds in stages (electrochemical and chemical stage), and with the participation of Ti^{3+} as reducing agent. In addition, due to the cyclic nature of the reactions, Ti^{4+} are not consumed, and act as catalyst.
- The CP particles obtained in the presence of Ti^+ have a spherical shape, with sizes ranging from 0.01 to 0.1 μm .

Authors' contributions

Abduali Bayeshov: supervised experiments; put forward the ideas of Cu^{2+} reduction in the presence of Ti^{4+} and explained its mechanisms; wrote the experimental part of the article. **Azhar Bayeshova:** collected the literary data; wrote the literary review, introduction and conclusions; suggested an experimental method; carried out calculations; participated in the development of the idea and interpretation of the results. **Umida Abduvaliyeva:** carried out electrolysis and analysis of the solutions; isolated CP and prepared them for analysis. **Aksulu Buketova:** collected literary data; carried out part of the experiments (electrolysis, analysis of the solutions); participated in calculations.

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