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Electrodeposition of composite coatings based on copper matrix included titanium dioxide in sulfuric acid solutions

Abstract. The process of reduction of Cu^{2+} from sulfuric acid solutions containing titanium dioxide as a dispersed phase (DP) was studied by electrolysis method. Composite electrochemical coatings (CEC) with a copper matrix with the inclusion of titanium dioxide were obtained. It has been established that with a change in the current density in the range of 50–300 A/m^2, the content of titanium dioxide in the CEC noticeably decreases. It is shown that an increase in the concentration of DP in the range of 5-20 g/l and the concentration of sulfuric acid from 50 to 250 g/l leads to an increase in the content of titanium dioxide in the coatings. It was also found that with an increase in the stirring rate (100–600 rpm) and the concentration of Cu^{2+} (5–50 g/l), the content of titanium dioxide in the coating increases. It is noted that at low concentrations of Cu^{2+} in the electrolyte, a loose powdery precipitate formed, which is associated with the occurance of cathodic processes at current densities above the limiting current and with the co-release of hydrogen. The release of hydrogen bubbles additionally contributes to the loosening of the precipitate, and also prevents co-deposition of titanium dioxide. It is found that a dense uniform coating is obtained upon polarization by a cathode pulsed current. The proportion of inclusion of titanium dioxide in the composition of the composite coating with a change in current density in the range of 50-400 A/m^2 reaches 2.1%. However, at current density above 400 A/m^2, copper is deposited in the form of a powder, and no coating is formed. The obtained CEC were identified by electron scanning microscopy, and their elemental composition was determined, confirming the presence of titanium dioxide. The micrographs show a uniform distribution of TiO_2 particles on the cathode surface.

Key words: composite coatings, matrix, dispersed phase, copper, titanium dioxide, current efficiency.

Introduction

During the cathodic reduction of metal ions with the inclusion of heterophase microparticles in the electrolyte, compact deposits are formed on the electrode surface, called composite electrochemical coatings (CEC).

Traditionally, CEC is obtained by cathodic deposition of a metal matrix from an electrolyte containing, along with metal ions, a dispersed phase (DP) of the added component in the form of a suspension. In order to improve existing methods, new approaches are being sought. For example, the creation of ultramicrocomposite coatings using pure monometals or their alloys. Sometimes attention is paid to obtaining porous and filter coatings. The use of self-regulating electrolyte suspensions, gel-like suspensions is noted. The applied methods include high-speed electrodeposition with mechanical activation of the electrode surface, sedimentation deposition of CEC and immersion methods. A wide range of coatings can be obtained by electroplating [1, 2].

Due to corrosion and wear resistance, as well as tribological properties, the dispersed phase TiO_2 is most often used as a hardener for a metal coating. It has been observed that a TiO_2 nanocomposite film on a Co matrix is approximately 30% harder than a microcomposite coating [3]. It has been established that the introduction of TiO_2 particles into the iron matrix leads to increasing the microhardness of the CEC [4]. Electrodeposition of nickel together with titanium dioxide (Ni-TiO_2) is used to improve the mechanical properties of cutting tools made of tungsten carbide [5].

There are coatings on a copper matrix that are strengthened by inclusions of graphene nanoplates, carbon nanotubes [6, 7]. The authors Rama Lingam S. et al. [8] used a copper substrate for electrodeposition of Cu-TiO_2 nanocomposite coatings, electrolysis was carried out in an acidic copper plating bath containing dispersed nanoscale titanium dioxide. The surface morphology and composition of nanocomposites were studied by scanning electron microscopy and energy dispersive X-ray spectral analysis (EDAX). The effect of surface-active substances (surfactants) during jet electrodeposition of composite coatings was investigated [9]. X-ray phase analysis showed that both sodium dodecyl sulfate (SDS) and hexadecyl trimethyl ammonium bromide (CTAB) reduced the grain sizes of the deposited coatings. The paper [10] presents the results of studying the corrosion behavior of a stoichiometric Cu–TiO_2 nanocomposite using self-propagating high-temperature synthesis (SHS).

Cătălina Iticescu [11] showed that composite coatings can be obtained on a copper matrix with nano-TiO_2 dispersed phases, the amount of TiO_2 embedded in the coatings is different and depends on the values of the current density and the number of nanoparticles in the electrochemical deposition bath. There are studies on the effect of pH on the thickness, grain size and morphology of the coating surface. The EDX results show that a metastable phase is formed during the synthesis [12]. There are works which researchers used pulsed current. For example, (Gulesin Yılmaz et al.) have shown that with pulsed current polarization, a higher percentage of inclusion is achieved compared to direct current [13]. A method for introducing a non-metallic phase up to 40% has also been proposed, which allows expanding the range of substances as a second phase [14].

A review of literature sources devoted to the study of the electrodeposition process of copper together with titanium dioxide showed that the resulting coatings are more resistant to corrosion than electroplated copper. However, we did not find any data elucidating the nature of the influence of the TiO_2 fineness, the electrolyte stirring rate, and the change in the electrolyte concentration at the current efficiency of the process. Calculations of the amount of inclusion are empirical, in this regard, they cannot fully cover the ongoing processes.

The purpose of our work is to identify the conditions for the formation of coatings on a copper matrix, with the inclusion of titanium dioxide as a dispersed phase, in copper-containing sulfuric acid solutions by electrolysis with cathodic polarization by constant and pulsed currents and to study the influence of the main parameters on the current efficiency.

Materials and methods

A schematic diagram of the installation for electrolysis is shown in Figure 1. The circuit includes an electrolyzer, laboratory power supply (MATRIX MPS-3005D, Matrix Technology Inc. China), magnetic stirrer (IKA RCT basic, IKA®-Werke GmbH & Co. KG, Germany), electronic scales (Model AS 310.X2, Radwag, Poland). The anode was a copper plate (99.99%), the cathode was titanium (99.70%). An aqueous sulfuric acid solution of $CuSO_4$ (ch. pr.) was used as an electrolyte. During electrolysis, copper was deposited on the cathode, which became the matrix. A coulometer – electrolyzer filled with a copper–containing sulfuric acid electrolyte, in which two copper electrodes were immersed, was sequentially connected to the electrochemical circuit.

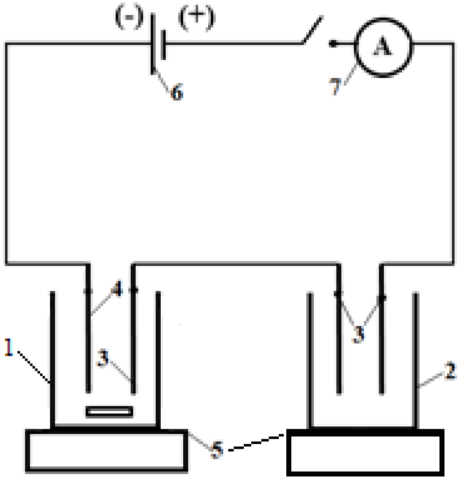


Figure 1 – Schematic diagram of the electrolysis unit: 1- electrolyzer; 2- coulometer; 3- copper electrodes; 4- titanium electrode; 5- magnetic stirrer; 6- power supply; 7-ammeter.

The essence of the experiments was that electrolysis was carried out with polarization by constant current and pulsed current. In this case, Cu^{2+} was reduced to Cu^0 in the form of a compact deposit on the surface of the titanium cathode. In order to obtain a composite coating, dispersed powders of rutile titanium dioxide (CRIMEA TiOx-230 brand) with an average particle size of 5 μm (dispersed phase) were introduced into the electrolyte. The concentration of titanium dioxide particles was changed in the range of 0-20 g/l. Before being added to the electrolyte, titanium dioxide was crushed in an ethanol medium using a Fritsch Pulverisette 6 (FRITSCH GmbH, Germany) mill in an 80 ml steel cup with steel balls 1 cm in diameter. The particle sizes were determined using the Laser Scattering Particle Size Distribution Analyzer (Horiba Particula La-960, HORIBA, Ltd, Japan) device with preliminary ultrasonic dispersion of powders in the form of a suspension in water.

Copper deposition on the cathode surface proceeds together with titanium dioxide, i.e. a composite coating is formed. However, determining the content of titanium dioxide in the composition of the coating seemed to be a rather difficult task. In this regard, a copper coulometer was sequentially connected to the electrochemical circuit. It is known and also experimentally established from the practice of copper electrolysis, that at a certain concentration of Cu^{2+} in solution and at optimal cathode current densities, copper deposition proceeds with a current efficiency of 100%; this phenomenon is used in coulometric analysis [15, 16]. Based on this, in our experiments, it was assumed that the exceeding 100% current efficiency of coating formation was associated with the co-deposition of the component – TiO_2. This approach can be explained as follows: in a coulometer, the current efficiency of copper deposition is 100%, in the main electrolyzer, copper is also deposited with a current efficiency of 100%. If the current efficiency exceeds 100%, the difference in the mass of the cathode will be the mass of titanium dioxide included in the coating composition. The obtained CEC "copper-titanium dioxide" was identified by physicochemical methods of analysis: scanning electron microscopy (scanning electron microscope JEOL JSM-6610LV, JEOL Ltd., Japan) and elemental analysis (energy dispersive X-ray fluorescence spectroscopy on an energy dispersive microanalysis system INCA Energy 450, mounted on a scanning electron microscope).

We note that sulphate (sulfuric acid) electrolytes containing Cu^{2+} are the simplest in composition and very stable in operation. The process was carried out for one hour (τ=1hour) at a temperature of 25°C. The influence of the main parameters of electrolysis, such as the concentration of titanium dioxide, the concentration of sulfuric acid, the concentration of Cu^{2+}, as well as the influence of the cathode current density and stirring rate on the process of coating formation, has been studied.

Results and discussion

The cathodic deposition of copper occurs according to the well-known reaction:

$$Cu^{2+} + 2e \rightarrow Cu^0 \quad E^0 = 0,34V$$

Under the conditions of our experiments, a compact copper deposit is formed on the cathode surface, and when titanium dioxide is included in the electrolyte in the form of a suspension, a copper-titanium dioxide composite coating is obtained. We believe that titanium dioxide is deposited together with Cu^{2+} in stages. First, the dispersed particles of titanium dioxide in the suspension state are transported; then they are retained on the cathode surface due to the magnitude of its charge or adsorption; after that, the particles are overgrown with precipitating copper.

The effect of the cathode current density in the range of 50-300 A/m^2 on the process of coating formation has been studied. The experiments were carried out at a titanium dioxide concentration of 10 g/l and at an electrolyte stirring speed of 300 rpm. With an increase in the current density at the cathode, the content of titanium dioxide in the composition of the composite coating noticeably decreases (Figure 2).

During electrolysis without TiO_2, the current efficiency of copper deposition was 100%. With the introduction of titanium dioxide into the electrolyte at a cathode current density of 50 A/m^2, the current efficiency of copper deposition is 102.7%, i.e. there is an excess of the CE (current efficiency) value, therefore, content of TiO_2 in the precipitate is 2.7%. At a current density of 300 A/m^2, the current efficiency is 100.6%, i.e. in this case, the content of TiO_2 in the cathode deposit is 0.6%. As was noted in the experimental methodology, if the current efficiency of coating formation exceeds 100%, the difference in the mass of the cathode after electrolysis will be the mass of titanium dioxide included in the coating composition.

With an increase in the concentration of TiO_2, its content in the cathode deposit also increases (Table 1). Changing the concentration of titanium dioxide suspension in the range of 5-20 g/l leads to an increase in the content of titanium dioxide in the coating from 0.7% to 1.3%. With an increase in the concentration of titanium dioxide to 10 g/l, the current efficiency of the coating increased abruptly, and in the concentration range of 10-20 g/l there is a slight gradual increase in current efficiency. We note that at higher concentrations of titanium dioxide, a decrease in the current efficiency is observed, due to the passivation of the electrode.

When the concentration of sulfuric acid changes in the range of 50 – 250 g/l, the content of TiO_2 in the coating increases from 0.4% to 1.6% (Figure 3).

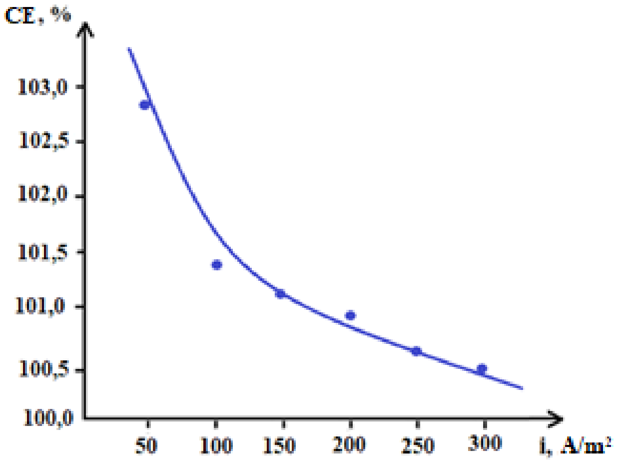


Figure 2 – Influence of cathode current density on deposit current efficiency: at H_2SO_4 – 100 g/l; Cu^{2+} – 40 g/l; TiO_2 – 10 g/l; τ=1 hour; T=25°C.

Table 1 – Influence of concentration of titanium dioxide (TiO_2) on current efficiency of the coating: at H_2SO_4 – 100 g/l; Cu^{2+} – 40 g/l; i=200 A/m²; τ=1 hour; T=25°C

TiO_2 concentration, g/l	0	5	10	15	20
Current efficiency, %	100.0	100.7	101.1	101.2	101.3

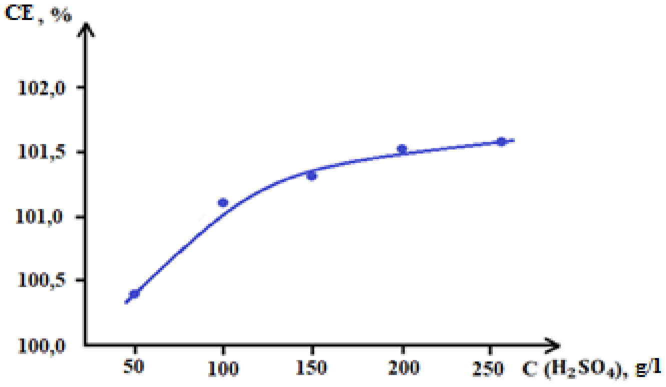


Figure 3 – Influence of sulfuric acid concentration on current efficiency of the cathode deposit: at Cu^{2+} – 40 g/l; TiO_2 – 10 g/l; i=200 A/m²; τ=1 hour; T=25°C.

The dependences of the current efficiency on the current density and on the concentration of sulfuric acid, shown in Figures 2 and 3, show that with an increase in the current density, the current efficiency of the coating decreases, and with an increase in the concentration of sulfuric acid, it increases. This can be explained by the fact that with an increase in the current density at the cathode, according to the Tafel equation, the potential value and, as a consequence, the charge value also changes. It is also known that the surface charge depends on the material, that is, on the value of the potential of the zero charge of the electrode.

When electrolysis is carried out without stirring, titanium dioxide is absent in the coating composition, since dispersed particles of titanium dioxide are delivered to the cathode surface only when the electrolyte is stirred due to sediment agitation. This effect is explained by the sedimentation rate of particles of different sizes. Changing the stirring rate of the electrolyte from 100 to 600 rpm contributes to the increase in the content of TiO_2 in the coating from 0.6% to 2.3% (table 2).

The process of CEC formation is influenced by a change in the concentration of Cu^{2+}. With their increase, the current efficiency increases significantly (Figure 4), i.e. the process of deposition of TiO_2 particles together with copper increases. If the concentration of Cu^{2+} in the electrolyte is low, then a loose powdery precipitate is formed, which is associated with the occurrence of cathodic processes at current densities higher than the limiting current. In addition, at a reduced concentration of Cu^{2+}, hydrogen is co-released at the cathode. Such a case is observed at a concentration of 1 g/l and below. In this case, part of the current is spent on the release of hydrogen. The current efficiency of cathodic deposit formation in this case is much lower than 100%. The release of hydrogen bubbles additionally contributes to the loosening of the precipitate, and also prevents co-precipitation of titanium dioxide. Therefore, figure 4 shows the data obtained at a concentration of copper ions of 5 g/l and higher. The joint release of hydrogen in this case no longer occurs (at a cathode current density of 200 A/m^2).

Table 2 – Influence of the electrolyte stirring rate on current efficiency of the coating: at H_2SO_4 – 100 g/l; Cu^{2+} – 40 g/l; TiO_2 – 10 g/l; i=200 A/m^2; τ=1 hour; T=25°C

V, rpm	0	100	200	300	600
Current efficiency, %	100.0	100.6	100.9	101.3	102.3

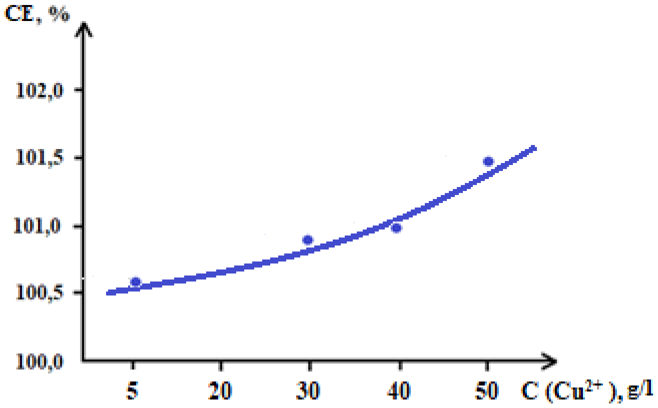


Figure 4 – Influence of Cu^{2+} concentration on the current efficiency of formation coating: at H_2SO_4 – 100 g/l; TiO_2 – 10 g/l; i=200 A/m^2; τ=1 hour; T=25°C.

As a result of electrolysis, a composite electrochemical coating containing copper and titanium dioxide particles was obtained. Figure 5 shows a titanium electrode: before electrolysis (a), covered with a copper film (b), covered with a copper film with inclusion of titanium dioxide (c). The results of the analysis confirmed the inclusion of titanium dioxide in the composition of the composite coating (Table 3).

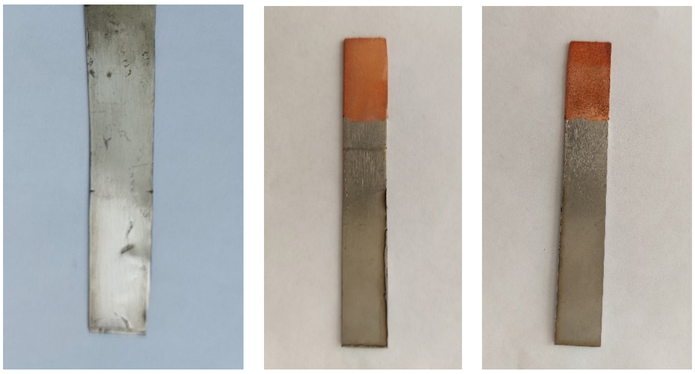
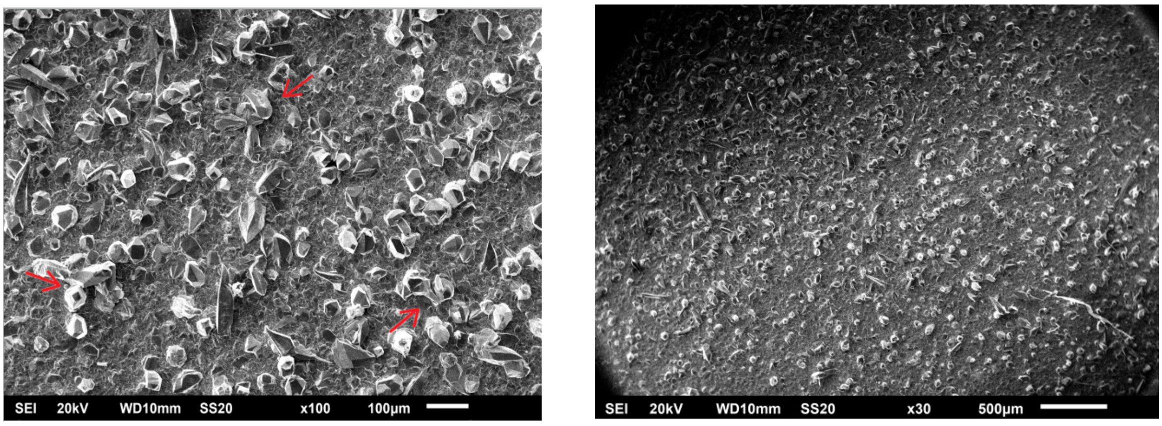

a) b) c)

Figure 5 – Photographs of titanium electrodes: before electrolysis (a), coated with copper (b), coated with a copper-titanium deposit (c). Coating (c) obtained at Cu^{2+} – 40 g/l; H_2SO_4 – 100 g/l; TiO_2 – 10 g/l; i=200 A/m^2; τ=1 hour; T=25°C.

Table 3 – The results of the elemental composition analysis of the obtained coating during constant current polarization

Spectrum	**Element composition, %**					
	O	**Al**	**Si**	**Ti**	**Cu**	**Total**
Spectrum	0.49	0.04	0.08	0.58	98.81	100.00
Spectrum	0.52	0.04	0.09	0.62	98.73	100.00
Spectrum	0.52	0.05	0.08	0.60	98.75	100.00
Average	**0.51**	**0.04**	**0.08**	**0.60**	**98.77**	**100.00**



a) b)

Figure 6 – Micrographs of the surface of a titanium electrode coated with a copper deposit containing TiO_2 at 100x (a) and 30x (b) magnification. Coatings were obtained at Cu^{2+} – 40 g/l; H_2SO_4 – 100 g/l; TiO_2 10 g/l; i=200 A/m^2; τ=1 hour; T=25°C.

Micrographs reflect the uniform distribution of TiO_2 particles on the cathode surface at 100-fold (a) and 30-fold (b) resolution (Figure 6).

In the case of polarization by a cathode pulsed current, data that characterize the effect of current density on the process of formation of copper coatings together with titanium dioxide particles were obtained. The experiments were carried out with variations in the cathode current density in the range of 50–400 A/m^2. It has been found that with increasing current density, the current efficiency of coating formation on the cathode increases (in the range of current densities of 50–200 A/m^2), and then decreases (Table 4). At cathode pulse current density values equal to 50, 100, and 200 A/m^2, the proportion of titanium dioxide inclusion in the coating composition was 0.04%, 0.31%, and 2.1%, respectively. At a current density value of 400 A/m^2 and higher, the current efficiency of the cathode coating decreases: copper was deposited in the form of a powder and partially passed into solution.

Table 4 – Influence of current density on current efficiency of the cathode coating in the presence of titanium dioxide (TiO_2): H_2SO_4 – 100 g/l; Cu (II) – 40 g/l; TiO_2 – 10 g/l; τ=1 hour; T=25°C

Current density, A/m^2	50	100	200	400
Current efficiency, %	100.04	100.31	102.1	100.43

As the research results showed, when polarized by a pulsed cathode current with a frequency of 50 Hz, a dense uniform coating is obtained. Figure 7 shows the cathode before electrolysis (Figure 7a) and after electrolysis (Figure 7b).

It has been established that under constant current polarization, the proportion of the dispersed phase TiO_2 included in the coating composition is 1.1% (at Cu^{2+} – 40 g/l; H_2SO_4 – 100 g/l; TiO_2 – 10 g/l; i=200 A/m^2; τ=1 hour; T=25°C).

When polarized by cathodic pulsed current, the proportion of the dispersed phase TiO_2 is 2.1% (at Cu^{2+} – 40 g/l; H_2SO_4 – 100 g/l; TiO_2 – 10 g/l; i=200 A/m^2; τ= 1 hour; T=25°C).

Micrographs of the coatings were obtained at 1000x (Figure 8a) and 3000x (Figure 8b) magnification.

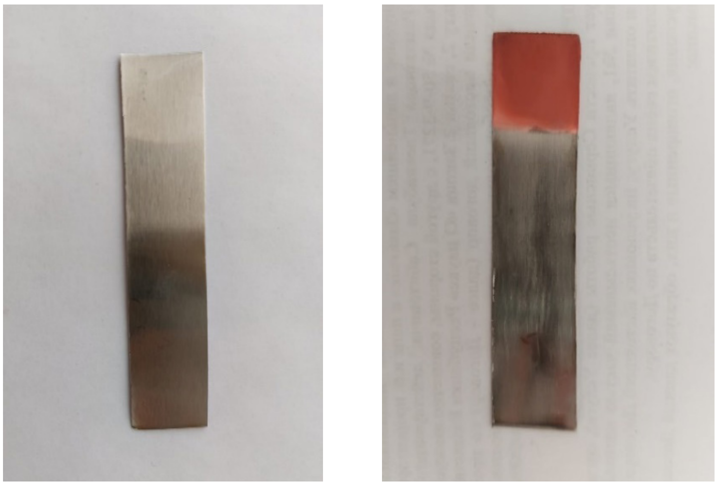
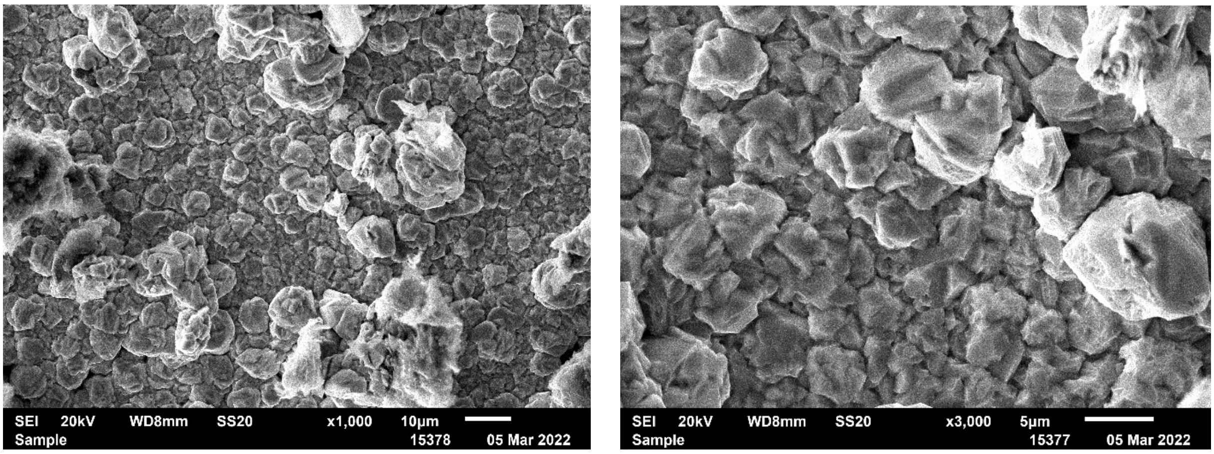

(a) (b)

Figure 7 – Photographs of cathodes: (a) – before polarization; (b) coating obtained by cathodic pulsed current polarization.



a) b)

Figure 8 – Micrographs of the coating obtained by polarization with a cathode pulsed current at 1000-fold (8a) and 3000-fold (8b) magnification. Coatings obtained at H_2SO_4 – 100 g/l; Cu^{2+}– 40 g/l; TiO_2 – 10 g/l i=200 A/m^2; τ=1 hour; T=25°C

Conclusion

Composite coatings deposited by electrochemical methods have advantages over compact metal coatings. The composition and uniformity of coatings are determined by the conditions of electrolysis. The main parameters of electrolysis that affect the quality of coatings are current density, electrolyte concentration, polarization duration, and stirring rate. In addition, the type of current used for the polarization process plays a certain decisive role. In this paper, it is proposed to use, along with constant current, the cathode pulsed current to obtain a coating. As a result, the inclusion fraction has increased significantly. Due to the fact that the dispersed non-metallic phase does not take part in electrode processes, it is usually difficult to determine the proportion of the included dispersed phase in the coating composition during electrolysis. It is proposed to use a coulometer connected in series in an electrochemical circuit, with its help it was possible to determine the proportion of the dispersed phase in the composition of the coating. The approach is new for determining the proportion of the dispersed phase included in the composition of the composite coating. According to the results of the experiments, the optimal composition of the electrolyte was established (Cu^{2+} – 40 g/l, H_2SO_4 – 100 g/l, TiO_2 – 10 g/l, V – 300 rpm, i=200 A/m^2), the content of TiO_2 in the composition of cathode copper exceeds 2.0%.

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