Electrodeposition of composite coatings based on cobalt, including refractory metals, allows obtaining coatings with a unique combination of physicochemical properties that cannot be achieved with other coating methods. The application of high-quality electrochemical composite coatings is only possible by establishing the characteristics of the electrolyte and electrolysis parameters. The characteristics of the scattering ability and specific electrical conductivity of Co-MoO₃-WO₃, Co-WO₃-ZrO₂, and Co-MoO₃-ZrO₂ electrolytes for depositing cobalt-based composite coatings have been established. The electrical conductivity values of the electrolytes for depositing cobalt-based composite coatings linearly increase with the temperature of the electrolyte, but their values at 25-30°C are sufficient for the deposition of high-quality coatings. It has been determined that within the current density range of 0.5-3.0 A/dm² for Co-MoO₃-WO₃ and up to 4.0 A/dm² for Co-MoO₃-ZrO₂ and Co-WO₃-ZrO₂, the scattering ability remains above 85%. The calculated activation energy of the electrical conductivity of complex electrolytes ranges from 22 to 29 kJ/mol, indicating the occurrence of mass transfer processes in the diffusion regime. Using insoluble inert stainless steel anodes in the technological process is justified.

**Keywords:** composite coatings; electrochemical deposition; cobalt, refractory metals; conductivity; scattering ability.

**UDC 621.357**

**TECHNOLOGICAL PARAMETERS OF GALVANICCHEMICAL PROCESSES OF FORMATION OF COBALT-BASED METAL OXIDE COMPOSITES**

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Received 21 March 2023; accepted 2 May 2023; available online 25 July 2023

**Abstract**

For the deposition of high-quality electrochemical composite coatings linearly increase with the temperature of the electrolyte, but their values at 25-30°C are sufficient for the deposition of high-quality coatings. It has been determined that within the current density range of 0.5-3.0 A/dm² for Co-MoO₃-WO₃ and up to 4.0 A/dm² for Co-MoO₃-ZrO₂ and Co-WO₃-ZrO₂, the scattering ability remains above 85%. The calculated activation energy of the electrical conductivity of complex electrolytes ranges from 22 to 29 kJ/mol, indicating the occurrence of mass transfer processes in the diffusion regime. Using insoluble inert stainless steel anodes in the technological process is justified.

**Keywords:** composite coatings; electrochemical deposition; cobalt, refractory metals; conductivity; scattering ability.
Introduction

Metal matrix composites are widely used by many branches of industry [1; 2]. The metals combined with the items of a different nature contribute to a considerable improvement of their operational properties [3]. Hence, the creation and the use of the composite electrolytic coatings (CEC) are technologically and economically advantageous production conditions. At the present time, the improved production technologies used to get such materials enable their use for construction-, automobile-, aviation-, shipbuilding and other industries that require to combine a high strength with microhardness increasing thus their wear resistance, and their high-temperature and corrosive media effect resistance [4]. Metal matrix composites are reinforced with the particles of a different shape and size and also with continuous and intermittent fibers [5–9].

The electrodeposition of the composite cobalt-based coatings especially with refractory metals enables the formation of the coatings with a unique combination of physical and chemical properties that cannot be obtained using other deposition methods [10; 11]. However, many aspects of process mechanisms have not been specified so far. The hypotheses that explain the kinetics and the reason for the joint electrodeposition of refractory metals with the iron family metals are built on the grounds of dispersion of the obtained experimental data and their interpretation relating to the same process. To explain the reasons for the joint deposition, several theories [12–14] have been suggested but none of them can explain the entire set of phenomena.

In recent years, substantial factual materials were collected that highlight the research data obtained for the electrodeposition conditions of composite coatings based on iron family metals that have an effect on their composition and properties [15–17]. However, only some of them have found a hands-on application. One of the reasons for the limited use of the electrolytic method of application of the coatings with such alloys and composites is a complicated monitoring of the electrolyte composition and the hindered process control.

Experimental technique

The investigations of the electrical conductivity, the dispersion capacity and the effect of the electrode material on the composition of electrolytic coatings [17] were carried out using the electrolytes [18], as given in Table 1. To prepare the electrolytes for the deposition of composite Co-MoO₂-WO₃, Co-MoO₂-ZrO₂, Co-WO₃-ZrO₂ coatings and other working solutions the reagents of a chemically pure grade and analytical grade have been used.

The electrical conductivity of electrolytes [18–20] was measured in the conductometric chamber using the E7-13 device to measure the electrolyte temperature \( T = 298 – 323 \) K. Prior to the experiment, the chamber was thoroughly washed, steamed and rinsed with the special solution used for experimental purposes. The measurements of \( R_\text{e} \) were repeated by filling the chamber with electrolyte to get the difference between the previous measurements and the subsequent measurements within 0.2%.

Composition of the electrolytes used for the deposition of composite cobalt coatings

<table>
<thead>
<tr>
<th>Electrolyte composition, mole/dm³</th>
<th>Co-MoO₂-WO₃</th>
<th>Co-MoO₂-ZrO₂</th>
<th>Co-WO₃-ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄·7H₂O</td>
<td>0.2</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Na₂MoO₄·2H₂O</td>
<td>0.16</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.08</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>Zr(SO₄)₂·4H₂O</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Na₃Ca₂H₂O₇·2H₂O</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>K₃P₂O₇</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Na₃SO₄</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>pH</td>
<td>9–10</td>
<td>9–10</td>
<td>9–10</td>
</tr>
</tbody>
</table>

The dispersion capacity was measured according to the National Standard or Derzhstandard 9.309-86 using the Hoole cell that enabled a more accurate simulation of the surface of a complicated profile. The effect of the nature of the anode material on the process of electrodeposition of composite coatings was determined using the plates made of stainless steel X18H10T, graphite, cobalt and tungsten [21]. The plates were arranged parallel to each other and connected with each other by the copper wire to provide a rigid fixation. The anodes were
subjected to the mechanical treatment with the sandpaper No0 and etched in the diluted sulfate acid or in the mixture of the sulfate and chloride acids in ratio 1:1 and rinsed with the distilled water.

Linear voltammetry was carried out using the potentiostat PI-50-1.1 equipped with the programmer PR-8 and a board for automatic online data recording with a specially developed program for digitizing the measurement results. Measurements were carried out in a standard electrochemical cell YASE-2 TU 25-05. A silver chloride half-element EVL-1M1 was used as the reference electrode. In the work, all potentials are calculated and presented relative to the normal hydrogen electrode.

Results and discussion

One of the preconditions for getting qualitative galvanic coatings is considered to be a high level of the electrical conductivity of electrolyte solutions ($\chi$) that contributes to the uniform distribution of the electric field in the electrolyte and to the reduction of the energy input and enables the formation of qualitative coatings. Based on the analysis of the experimentally defined temperature dependence of electric conductivity (Fig.1) we can state that the integrated citrate-diphosphate electrolytes used for the deposition of the cobalt-based composite electrolytic coatings (CEC) can have a sufficiently high dispersion capacity.

With rising temperature, the electrical conductivity of electrolyte solutions is predictably increased due to a decrease in the medium viscosity. It contributes to an increase in the operating current density and partial dehydration of the ions (a decrease in the radius of a hydrated ion) and an increase in the degree of dissociation.

The activation energy of the electrical conductivity of integrated electrolytes that was calculated using the graphic analysis of the temperature dependence of electrical conductivity varies in the range of 22 to 29 kJ/mole and it is indicative of the mass-transfer processes in the diffusion mode.

Since the experimentally defined values of the electrical conductivity of the solutions used for the deposition of test coatings are within $\chi = 0.055$–0.07 0m$^{-1}$m$^{-1}$, the temperature interval of 25 to 30 °C can be considered as optimal for the deposition of the cobalt-based composite electrolytic coatings.

One more important process parameter of the electrochemical deposition of composite coatings is the distribution of local rates on the substrate surface and in its turn, it is defined by the distribution of current on the treated surface [23; 24]. With regard to this process such a parameter is the dispersion capacity (DC) and the obtained data of it show that the dispersion capacity of the electrolytes used for the deposition of composite Co-MoO$_x$-WO$_x$, Co-MoO$_x$-ZrO$_2$ and Co-WO$_x$-ZrO$_2$ coatings is decreased with an increase in the...
current density (Fig. 2). Such a behavior of the cobalt-based CECs can be related to the amorphization of the structure of composite coatings. However, for the current density range of 0.5 to 3.0 A/dm$^2$ for Co-MoO$_x$-WO$_x$ and up to 4.0 A/dm$^2$ for Co-MoO$_x$-ZrO$_2$ and Co-WO$_x$-ZrO$_2$ the value of this parameter still exceeds 85%.

The obtained CECs of the Co-Mo-ZrO$_2$ composition have a uniform opaque gray-dark color only for the first and second cathode sections that were arranged closer to the anode. The darkened edges of the coating can be noticed due to the exceeded limiting current density on those sections and excessive hydrogen release.

The electroconductive dope of 0.5 mol/dm$^3$ Na$_2$SO$_4$ was added to the working electrolyte to improve the parameter of the dispersion capacity, i.e., to contribute to a more uniform metal distribution on the cathode surface.

The electrodeposition of the cobalt-based composite coatings from citrate-diphosphate electrolytes is sensitive to a change in their composition, therefore the anode materials should have an appropriate corrosion resistance with no oxidation reactions of electrolyte components that result in a change of the electrolyte composition. To carry out galvanic processes, the anodes that are usually used for this purpose should be made of the same metal as the coatings. However, in the case of the electrolytic deposition of multicomponent coatings the selection of the soluble anode made of several metals is complicated by a different rate of the dissolution of available components that results in the enrichment of the electrolyte only with one type of ions.

To define the performances of electrode processes we obtained polarization dependences for different anode materials. Since the recovery of metals is not a single process such dependences are summarized and these are characterized by a simultaneous behavior of all anode reactions.

The overwhelming majority of scientists carry out experimental investigations using the inert electrode, giving preference to platinum or stainless steel. From the standpoint of the need for the determination of the effect of the concentration of alloy-forming components on the coating composition such an approach is absolutely justified because the inert electrodes have no effect on the content of the electrode-active particles in the electrolyte [25]. The specific features of the electrodeposition of the cobalt-based composite coatings embrace the differences not only in the behavior of cathode reactions but also those in the behavior of anode reactions of the given metals. Hence, the use of soluble anodes in this case is the subject of an extensive solitary investigation. However, this scientific paper proves the possibility of the use of the inert anodes made of stainless steel and substantiates the ranges of the density of anode currents under which the behavior of the anode reaction has a minor effect on the structure and the number of electrode-active particles.
During the deposition of composite Co-MoOₓ-WOₓ, Co-MoOₓ-ZrO₂, Co-WOₓ-ZrO₂ coatings the anode potential on the X18H10T steel is biased in the positive direction with an increase in the cathode current density and it is within 1.9 V in the current density investigation range (2.0–12.0 A/dm²) (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Coatings</th>
<th>Polarization current density iₓ, A/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Co-MoOₓ-WOₓ</td>
<td>1.42</td>
</tr>
<tr>
<td>Co-WOₓ-ZrO₂</td>
<td>1.48</td>
</tr>
<tr>
<td>Co-MoOₓ-ZrO₂</td>
<td>1.43</td>
</tr>
</tbody>
</table>

The studies of the anode behavior of different electrode materials in the electrolyte solutions used for the deposition of composite coatings allow us to draw the following conclusion. The unavailability of any active processes on the X18H10T steel in the range of the potentials up to +0.8 V for composite Co-MoOₓ-WOₓ coatings and +1.2V for Co-MoOₓ-ZrO₂ and Co-WOₓ-ZrO₂ coatings confirms the possibility of the use of those anodes as inert anodes.

As is known [26], the use of insoluble anodes allows for an improved quality of coatings and an increased efficiency of the cathode process. The cobalt anodes are dissolved with the formation of Co²⁺ at a high rate with a minor polarization and it is indicative of an abrupt increase in the current density on the voltamperograms (Fig.3).

Fig.3. Anode voltamperograms for cobalt (1), graphite (2), X18H10T steel (3) and zirconium (4) electrodes in the electrolyte solution used for the formation of composite Co-MoOₓ-WOₓ (a), Co-MoOₓ-ZrO₂ (b) and Co-WOₓ-ZrO₂ (c) coatings; s = 2·10⁻³ V/s
The use of soluble anodes made of cobalt can only provide the compensation of the cobalt consumption during the electrolysis and the extension of the electrolyte resource [24; 27]. However, on the other hand it results in the violation of the concentration ratio of complexing agents in the solution because it is impossible to attain an appropriate rate of the dissolution of cobalt with refractory metals (zirconium) using composite anodes. The use of soluble anodes leads to the electrolyte alkalinization and it results in a reduction of its resource. It can be explained by the formation of hydroxide ions in the combined cathode reaction of the hydrogen release and the impossibility to compensate their effect on the value of anode reactions because there is no oxygen release on the soluble anode that could acidify the solution.

The anode polarization dependences for the graphite anode (Fig.3, dependence 2) have the plateau up to the potentials of 0.7 to 0.9 V for such CECs as Co-MoO$_x$-WO$_x$ and Co-MoO$_x$-ZrO$_2$ and it is indicative of the impossibility of their use as the anode material.

During the electrolysis, the tungsten anode is coated with a thick oxide film and it acts as an insoluble anode and appropriate measures should be taken for its activation, in particular the component composition of the electrolyte should be changed by introduction of activator ions, etc. Undoubtedly, it affects the process productivity and the quality of coatings.

Hence, it is reasonable to use inert anodes made of stainless steel for the deposition of composite Co-MoO$_x$-WO$_x$, Co-MoO$_x$-ZrO$_2$ and Co-WO$_x$-ZrO$_2$ coatings. It should be noted that the anode current density, as shown in Fig.3, should be maintained at a level of 0.2 to 0.3 A/dm$^2$, and the anode-to-cathode area ratio should be as $S_A : S_C = 1:10$ [27].

**Conclusion**

The dispersion capacity and the specific electric conductivity of the electrolytes used for the deposition of composite Co-MoO$_x$-WO$_x$, Co-MoO$_x$-ZrO$_2$ and Co-WO$_x$-ZrO$_2$ coatings have been determined. The electric conductivity is increased linearly with an increase in the electrolyte temperature, but its values are sufficient for the deposition of qualitative coatings onto the parts of a complicated configuration.

The use of the insoluble inert anodes made of stainless steel for the technological process has been substantiated. It was shown that the use of combined active anodes is impossible due to a different dissolution rate of alloy-forming metals co-depositing to composite coatings.

**References**


