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Original scientific paper

Electrochemical obtaining of rhenium-molybdenum alloys

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Abstract

Based on the study of current-voltage dependencies during the co-deposition nt electrical reduction of rhenium and molybdenum from sulfuric acid on a Pt electrode, conditions for deposition of alloy nanocoatings of the Re-Mo system were established. The influence of various factors, such as the content of components in the electrolyte, current density, temperature, acidity of solutions, etc., on the composition and quality of coatings was studied. It was established that with an increase in the content of rhenium in the electrolyte and an increase in current density, the content of rhenium in the alloy is increased. The composition and morphology of Re-Mo thin films electrodeposited on a platinum electrode were analyzed. The phase composition of the obtained films was determined by XRD using a diffractometer, and the study of the morphology of Re-Mo films on platinum and nickel substrates was performed using a scanning electron microscope. Based on this study, the optimal conditions for the deposition of molybdenum with rhenium and the required composition of the electrolyte were selected. For obtaining rhenium-molybdenum alloys containing 50-80 wt.% Re, the following electrolyte composition can be recommended: 0.0015M Na_2MoO_4 + 0.0035M $KReO_4$ + 2M H_2SO_4, pH 0.4; t = 75 ℃*, the electrode - Pt.*

Keywords

Binary alloys; rhenium alloy, thin coatings, electrochemical deposition; electrolytic bath composition

Introduction

The unique physical and chemical properties of rhenium make this metal promising for use in various high-tech industries, such as aviation, rocket engines, nuclear power engineering, electronics, biomedicine, and heterogeneous catalysis [1-10].

Studies of the process of electrodeposition of rhenium and its alloys are primarily of practical but also theoretical interest [11-15]. The practical significance of research in this area is associated mainly with the growth in the production of rhenium and, consequently, with the need to address the issue of the optimal technology for the separation of rhenium from solutions in the form of pure metal or alloys. In addition, it is required to find the possibilities of using rhenium and its alloys as galvanic coatings for various purposes [16-18].

From the theoretical point of view, the process of electrodeposition of rhenium and its alloys is also of interest, since rhenium, like many other refractory metals, is released from the anions (ReO_4^-), and the mechanism for the separation of metals from anions is complex and insufficiently studied. Therefore, the data obtained on the example of rhenium may also be useful for the analysis of similar processes.

Rhenium is a strong, ductile, refractory metal with a hexagonal close-packed crystal structure. It has the second-highest melting point among all metals (after W) of 3157 to 3181 °C. Molybdenum, in turn, is a very universal refractory metal exhibiting high melting point and high heat resistance. In addition, it could be easily mechanically processed. Molybdenum and rhenium in pure forms on the cathode can be obtained only with low current efficiency [19-27]. Rhenium has a unique effect on lowering the transition temperature of tungsten and molybdenum. The mechanism of action of rhenium on these metals has not yet been fully elucidated. Rhenium is characterized by very high solubility in transition metals. Alloys of rhenium with molybdenum and tungsten are of great practical interest since rhenium has an exceptional influence on their deformability and mechanical properties.

Previously [17,18,28], we obtained coatings of rhenium alloy with chalcogens by the electrochemical method. As is known from the literature, rhenium can be deposited from both acidic and alkaline electrolytes [9-14].

The purpose of this work is the electrochemical obtaining of new nanomaterials based on Re-Mo alloys on various substrates. For this purpose, a study of cathodic processes during the reduction of molybdenum and rhenium in the sulfuric acid on Pt and Ni electrodes is carried out. In addition, the possibility of obtaining thin Re-Mo alloy coatings from sulfuric acid containing various concentrations of Na_2MoO_4 and $KReO_4$ as metallic precursors at pH 0.4 and 75 °C is studied in detail. The optimization of electrodeposition operation parameters for the alloy, as well as characteristics of the obtained Re-Mo deposits, are also discussed.

Experimental

Preparation of solutions and electrolysis mode

The following reagents were used in the given work: $KReO_4$ (99 %), H_2SO_4 (99 %), Na_2MoO_4 (98 %), HNO_3 (99 %), $(NH_2)_2CS$ (99 %), $SnCl_2 \cdot 2H_2O$ (98 %), H_3PO_4 (99 %), CrO_3 (99 %), $Na_2SO_3 \cdot 7H_2O$ (98 %), all by Sigma-Aldrich.

The indicated reagents were purified before use. Hydrochloric and sulfuric acids (chemically pure) were exposed to double distillation. To obtain the Re–Mo alloy, the electrolyte was prepared as follows: the given amounts of $KReO_4$ and Na_2MoO_4 were loaded into the volumetric flask, followed by their dissolution in the concentrated H_2SO_4 in the required amount, and diluted with distilled water to a certain volume. This solution served as the stock solution, and all used solutions were prepared by further dilution of a certain amount of this solution. $KReO_4$ is very slightly soluble in acid, so solutions were prepared by heating up to 75 °C.

In order to determine the chemical and phase composition and microstructure of the obtained alloys, platinum and nickel electrodes having a constant geometrical area of 4 cm^2 were used, while galvanostatic and potentiostatic depositions were performed.

Polarization measurements were carried out using the platinum cathode, with a surface of 0.15 cm^2, soldered into a glass tube. Before immersion in the solution, the electrode was mechanically polished, degreased, boiled in 30 % nitric acid, and washed with an appropriate electrolyte. Before use, the nickel electrode was mechanically grinded, degreased with Vienna lime (used for cleaning and polishing metal, having the composition: CaO, MgO and Fe_2O_3), electrochemically polished, and then washed twice with distilled water. During polarization measurements, a platinum working electrode was also used. An Ag/AgCl-KCl electrode was used for polarization measurements as the reference electrode. The auxiliary electrode was a platinum wire with a surface several times higher than the surface of the working electrode.

In order to study the kinetics of electrochemical processes during the co-electrodeposition of rhenium and molybdenum, the cyclic voltammetry technique was used, involving an IVIUMSTAT potentiostat. The polarization curves were recorded using a glass cell equipped with a 50 ml glass jacket and with the platinum electrode used. To check the reproducibility of the results, each experiment was carried out in duplicate. The temperature in the electrolytic cell was maintained constant with an accuracy of 0.1 °C by a U-10 thermostat. Current output was detected with a copper coulometer by weighing method and calculated regarding the composition of deposit. The pH of solutions was determined using pH/mV/TempAZ86551 equipment.

Determination of thin alloy coatings composition

The composition of cathodic Re–Mo alloy deposits was determined as follows. The cathodic deposit obtained by the electrochemical method was dissolved in 10 ml of concentrated nitric acid under heating. After repeated evaporation in a water bath, 1.67 M (5 N) H_3PO_4 solution was added. Rhenium was separated from molybdenum by extraction with isoamyl alcohol and then rhenium and molybdenum were determined by spectrophotometry taking into consideration the thiourea complex of rhenium and the thiocyanate complex of molybdenum using a SPECORD-50 PLUS equipment. Then, it was photometrically measured to the zero solution at 390 nm in a cuvette 1×1 cm. The content of rhenium was determined by a calibration curve built using standard solutions of rhenium.

In a flask with a capacity of 50 ml, a certain amount of a Re-containing solution was added, 10 ml of concentrated hydrochloric acid, 10 ml of a 5 % aqueous solution of thiourea, 2 ml of a 20 % solution of tin chloride in concentrated hydrochloric acid, bring to the mark with distilled water and mix. After an hour, solutions are photometered on SPECORD 50 PLUS instrument using a blue light filter in cuvettes 1-10 cm relative to distilled water.

The three-electrode cell contained the electrode under study, an auxiliary platinum electrode with an area of 4 cm^2, and a silver chloride reference electrode (Ag/AgCl-KCl). To study the structure and composition of deposited films, deposition was carried out on Pt and Ni substrates with an area of 4.0 cm^2. Platinum electrode was used as an anode for potentiostatic and galvanostatic depositions. The working temperature for electrodeposition was 75 °C and the deposition time was 60 min. To study the morphology of films on platinum and nickel substrates, the electrode surface was examined on a JEOL JSM7600F scanning electron microscope at various magnifications and, accordingly, was subjected to elemental analysis using an Oxford X-MAX 50 detector. X-ray diffraction analysis of the obtained films was carried out on a DRON-5 setup with Cu K α-radiation. The films were obtained using galvanostatic mode in stationary conditions. For chemical analysis, the cathode deposit was dissolved on heating in concentrated HNO_3. The amount of rhenium and molybdenum was determined separately by the thiourea complex using the colorimetric method on SPECORD 50 PLUS instrument.

Results and discussion

In order to study the kinetics of the co-electrodeposition of Re with Mo, the obtained polarization curves of individual components were compared with those obtained during their co-deposition. For this purpose, the influence of various factors on the electrodeposition of rhenium and molybdenum in the test solution was studied.

The potentiodynamic polarization curve, presenting the reduction of molybdate ions from the investigated solution, is shown in Figure 1a. In the potential range of -0.1 to 1.0 V *vs.* Ag/AgCl, with the increasing negative value of electrode potential, there was an increase in the cathode current density of the reaction of incomplete reduction of molybdate ions.

As is known from the literature, molybdenum is deposited from both acidic and alkaline electrolytes [19-27]. In this work, the choice of sulfuric acid was made based on the fact that it is possible to obtain high-quality molybdenum deposits from this electrolyte, while it is not always possible to obtain high-quality films from molybdate solution in a very acidic electrolyte using sulfuric acid. Also, it was established by preliminary experiments that high-quality films can be obtained from sulfuric acid even at very low concentrations of molybdenum in the electrolyte. For this purpose, cathode processes were studied at different concentrations of molybdenum in sulfuric acid on a Pt electrode. Figure 1b shows the cyclic polarization curves presenting the reduction of molybdenum from molybdate solution in a very acidic electrolyte using sulfuric acid at various scan rates.

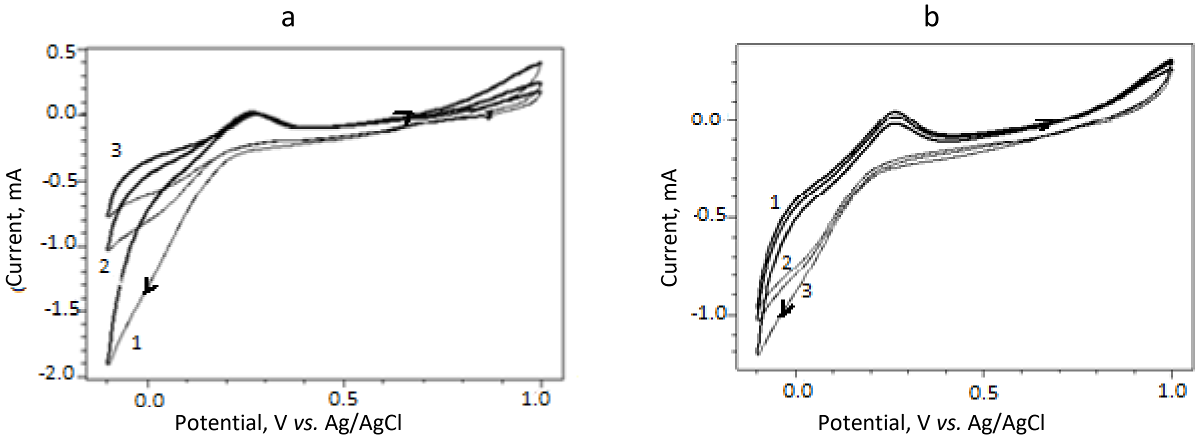

Figure 1. *Cyclic voltammograms of molybdenum deposition on Pt electrode in 2 M H_2SO_4, pH 0.4, 75°C at: (a) scan rate 5 mV s^{-1} and following concentrations of Na_2MoO_4 (1) 0.02 M; (2) 0.015 M; (3) 0.0015 M and (b) 0.0015 M Na_2MoO_4 at different cycles (1-3)*

Usually, after immersing the Pt-electrode in sulfuric acid for 30 minutes, the electrode potential takes a constant value equal to 0.50±0.05 V, which does not change with a change in the concentration of Mo in the solution. The main role in establishing the stationary potential is played not by the equalization of the concentration ratios in the cathode layer but by the balance between the electrode surface and solution, due to the presence of an oxide film and sparingly soluble compounds on the cathode surface.

As is known from the literature, rhenium electrolytes are acidic electrolytes. The electrochemical behavior of rhenium in sulfuric acid solutions was studied in [2,3]. During electrolysis from acidic rhenium-containing solutions, depending on the conditions of electrolysis and the composition of the electrolyte, coarse-grained or fine-grained deposits of rhenium are deposited on the cathode. Figure 2 shows the polarization curves of rhenium deposition on the Pt electrode from sulfuric acid. As is known from the literature [6-8], in the sulfuric acid, rhenium is in the form of Re O_4^- and its reduction probably consists of several separate processes. The discharge of Re O_4^- ions is carried out in stages, and each of the stages of the formation of intermediate products is undoubtedly characterized by a certain electrode potential. This electrode potential becomes more negative in the process of reduction, which can also contribute to the convergence of deposition potentials of rhenium and molybdenum. Thus, the reduction of rhenium in strongly acidic electrolytes proceeds in stages through the formation of an intermediate oxide film, as evidenced by the presence of red and blue precipitates in the resulting film. Figure 2a shows the polarization curve of rhenium deposition from the sulfuric acid electrolyte, while Figure 2b shows rhenium deposition from sulfuric acid at different concentrations of rhenium in the sulfuric acid.

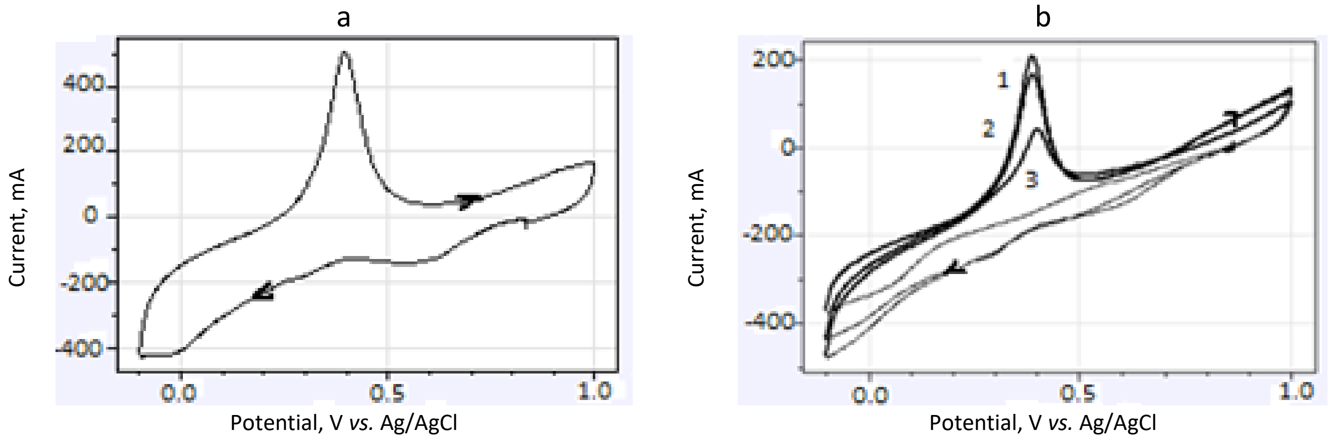

Figure 2. *Cyclic voltammograms (5 mV s^{-1}) of rhenium deposition on Pt electrode in 2 M H_2SO_4, pH 0.4, 75 °C and presence of: (a) 0.00084 M $KReO_4$ and (b) various concentrations of $KReO_4$ (1) 0.00069 M; (2) 0.0035 M; (3) 0.035 M*

The influence of various factors on the co-deposition of rhenium and molybdenum was also studied. Current density, temperature, pH, rhenium and molybdenum concentration in solution, sulfuric acid concentration, and electrodes were varied in order to obtain better quality and nanolayers. It turned out that all these factors affect the composition and quality of the alloy coating in different ways. Based on these studies, the optimal conditions for the deposition of solutions of molybdenum with rhenium and the required composition of the electrolyte were selected.

Figure 3 shows the polarization curves during the co-deposition of rhenium with molybdenum from a sulfuric acid solution. As shown in Figure 3, the alloy formation curves differ from the polarization curves of individual components shown in Figures 1 and 2. While the polarization curves of rhenium show one wave, these curves of the alloy show two sections of the limiting currents. It is possible that during co-electrodeposition, the reduction of rhenium and molybdenum is accelerated, as rhenium catalyzes the reduction of molybdenum. This indicates once again that the reduction potentials of rhenium and molybdenum are approaching each other [19,21]. With such an arrangement of polarization curves, the potentials for the realization of components converge, and depolarization of both components occurs when they are released into the alloy due to the heat of the formation of the compound or solid solution. Indeed, the analysis of cathodic deposits at current densities of 10 to 35 mA cm^{-2} showed deposits close to the corresponding compositions of solid solutions or Re-Mo compounds. The proof that compounds or a solid solution based on the Re-Mo alloy are formed on the cathode follows directly from the cyclic polarization curves shown in Figure 3.

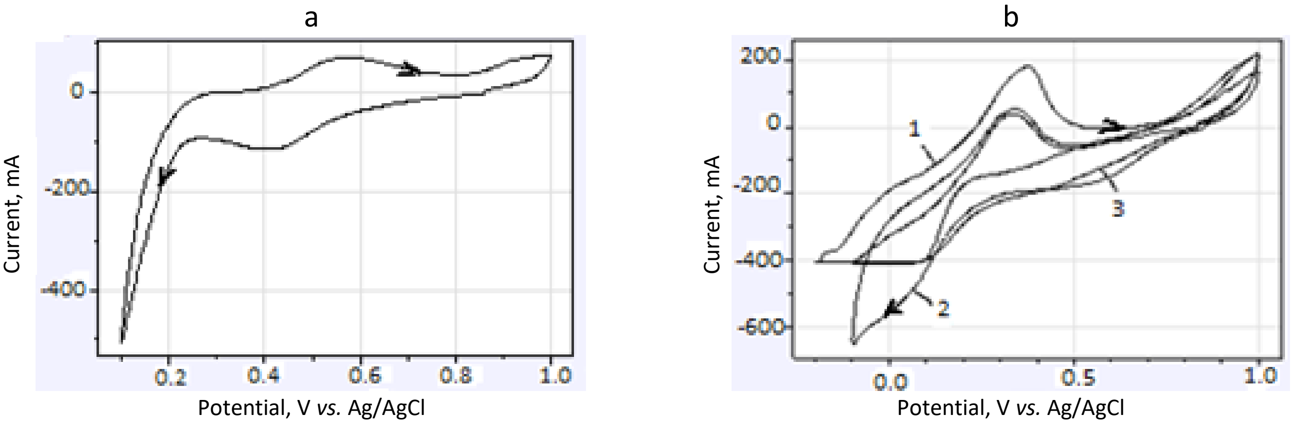

Figure 3. *Cyclic voltammograms (5 mV s^{-1}) of rhenium and molybdenum co-deposition on Pt electrode in 2 M H_2SO_4, pH 0.4, 75 °C, in presence of 0.0015M Na_2MoO_4 and: (a) 0.035M $KReO_4$; (b) various concentrations of $KReO_4$ (1) 0.035 M; (2) 0.0035 M; (3) 0.00069 M*

As can be seen from Figure 3, on the current-voltage curves of the anodic part of rhenium and molybdenum, respectively, almost one oxidation wave is observed related to the oxidation of rhenium and molybdenum. The wave observed at the potential of 0.3 V is undoubtedly due to the anodic dissolution of rhenium, and the wave at the potential of 0.4 V is due to the anodic dissolution of molybdenum. Thus, the obtained data prove again that in the co-deposition of rhenium with molybdenum, the main role is played by the chemical activity of rhenium, associated with its tendency to reduce. In this case, the deposition of both components, forming the alloy is accompanied by depolarization. Depolarization during the release of rhenium into the alloy is associated with the formation of a chemical compound of molybdenum with rhenium.

Table 1 shows the data on the dependence of the alloy composition on the concentration of rhenium in the electrolyte. As can be seen from Table 1, with an increase in the concentration of rhenium in the electrolyte, the content of rhenium in the alloy increases. The chemical composition of alloy was determined both chemically and as a result of EDX. High-quality alloys are obtained at the temperature of 75 °C and 0.004 M $KReO_4$ in the electrolyte.

Table 1. *Dependence of the composition of Re–Mo alloy on the concentration of rhenium in 2 M H_2SO_4 containing constant concentration of molybdenum. Alloy is formed on Pt electrode at current density i_k = 25 mA cm^{-2} and 75 °C*

Electrolyte concenration, M			Content, wt.%		Deposit appearance
$KReO_4$	Na_2MoO_4	H_2SO_4	Re	Mo	
0.003	0.0015	2	69	31	Dark-grey, smooth
0.0035	0.0015	2	70	30	Dark-grey, smooth
0.004	0.0015	2	72	28	Dark-grey, smooth
0.0045	0.0015	2	76	24	Dark-purple, smooth
0.005	0.0015	2	78	22	Dark-grey, smooth

The study of the Re-Mo electrochemical deposition process shows that the composition and quality of the resulting coatings mainly depend on the current density. It has been shown in Table 2 that with an increase in current density from 5 to 30 mA cm^{-2}, the amount of rhenium in the alloy increases from about 50 to about 80 wt.%.

As expected, the composition and quality of Re-Mo alloys are strongly affected by temperature. It has been established that the rhenium content in the alloy increases with an increase in temperature. With an increase in temperature, the value of the limiting current increases, probably due to diffusion changes in the near-cathode sheath. High-quality deposits in the form of thin films are obtained at the temperature of 75 to 80 °C, and at the temperature of 25 to 45 °C, loose deposits of Re-Mo alloy are obtained on the cathode. Table 3 shows the data on the dependence of the composition of the alloy on the temperature of the electrolyte.

Table 2. *Dependence of the composition of Re–Mo alloy on the current density of Pt electrode in 2 M* H_2SO_4 *containing constant concentrations of molybdenum and rhenium, at 75 °C*

Electrolyte concentration, M			Content, wt.%		Current density, mA cm^{-2}	Deposit appearance
$KReO_4$	Na_2MoO_4	H_2SO_4	Re	Mo		
0.0035	0.0015	2	52	48	5	dark-grey, smooth
0.0035	0.0015	2	58	42	15	dark-grey, smooth
0.0035	0.0015	2	62	38	20	dark-grey, smooth
0.0035	0.0015	2	69	31	25	dark-grey, matt
0.0035	0.0015	2	76	24	30	dark-grey, smooth

Table 3. *Dependence of the composition of Re–Mo alloy on temperature of the electrolyte composed from 2 M* H_2SO_4 *and constant concentrations of Re and Mo, during deposition on Pt electrode at current density* j_k *= 25 mA* cm^{-2}

Electrolyte concentration, M			Content, wt.%		Temperature, °C	Deposit appearance
$KReO_4$	Na_2MoO_4	H_2SO_4	Re	Mo		
0.0035	0.0015	2	50	50	25	dark-grey, smooth
0.0035	0.0015	2	56	44	45	dark-grey, matt
0.0035	0.0015	2	60	40	60	dark-grey, smooth
0.0035	0.0015	2	69	31	75	dark-grey, matt
0.0035	0.0015	2	75	25	85	dark-grey, smooth

The paper also considers the influence of the duration of deposition at different current densities and electrolyte pH on the properties of the rhenium-molybdenum alloy. It has been established that changes in the pH of the solution significantly affect the kinetics of cathodic reduction of Re-Mo alloys, the quality of the deposit, and the effective current efficiency. In acidic environments (up to pH 3.0), the release of metal is accompanied by the intense release of hydrogen, which reduces the current efficiency and the content of molybdenum in the alloy and worsens the quality of the precipitate. Increasing the pH of the solution above 6.0 makes it possible to increase the content of molybdenum in the alloy but reduces the current efficiency from 40 to 5 %. A study of the surface of coatings of Re-Mo alloys obtained by co-deposition from electrolytes with different pH values showed that uniform, shiny coatings are formed at pH from 0.2 to 3.0.

It was found that at a low concentration of one of the components, the alloy is a solid solution based on the second component. Therefore, in this case, when studying the kinetics and mechanism of molybdenum deposition, the main attention was paid to those factors that contribute not only to obtaining high-quality deposits but also significantly shift the potential of a more noble metal to the negative side (or the deposition of a more noble metal is accompanied by high polarization).

The polarization curves of Re-Mo alloys using a Ni working electrode are presented in Figure 4. As can be seen from the figure, the cathodic reduction of the Re-Mo alloy is located in the region of more positive potentials than the potentials of deposition of individual elements. With the shift of the cathode curve to the region of more positive potentials, the value of the limiting current increases. A similar effect is explained by the release of energy during the formation of a chemical compound.

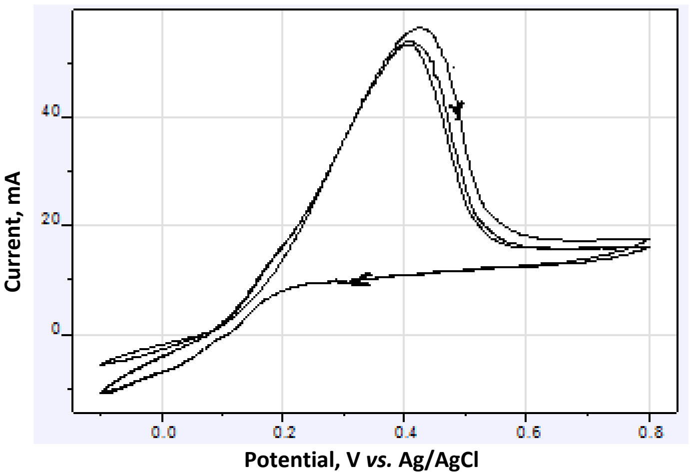

Figure 4. *Cyclic voltammograms (5 mV s^{-1}) of Ni working electrode in 2 M H_2SO_4, 0.0015 M Na_2MoO_4 and 0.0035 M $KReO_4$, pH 0.4; 75 °C*

Chemical and X-ray diffraction analysis established that at a potential of -0.1 V, an alloy is obtained on the cathode, the composition of which corresponds to the Re-Mo.

Morphologies of Re-Mo films deposited on platinum substrates were studied by a scanning electron microscope. It was established generally that depending on the material of the substrate, thin coatings with different compositions and sizes were obtained on the cathode when prepared at the same experimental conditions. However, coatings with grain sizes of 80-150 nm were obtained on Pt substrate electrode. Examples of the SEM image and elemental composition of Re-Mo film deposited on Pt substrate are shown in Figure 5 and Figure 6, respectively. Upon thorough investigation, a structure similar to nanostructure and formation of nanosized islets on a platinum sample is observed. Islets do not have a certain shape, but they have forms of an egg, ellipse, and various other shapes.

X-ray pattern of Re-Mo thin film deposited on Pt electrode and annealed at 500 °C for 2 hours is presented in Figure 7. It was found that depending on the electrolyte composition and current density during electrolysis, the substances comprising one phase are obtained. At optimum deposition conditions, the obtained Re-Mo thin films on a platinum electrode contain oxide compounds. To purify the composition of films from various oxides, the substances obtained electrochemically in Re-Mo system were annealed at 500 °C for 2 hours and an X-ray pattern was recorded. Intensity of the peaks becomes much more visible after annealing. This may be due to the annealing of oxides in films.

It follows from the SEM data that the film consists of 76.9 wt.%, Re, and 23.1 wt.% Mo. Figure 6 shows the microstructure of Re-Mo thin coatings obtained by the electrochemical method.

In addition to potassium perrhenate and sodium molybdate, ammonium sulfate, citric or boric acid were also introduced into the composition of electrolytes for the deposition of rhenium alloys with molybdenum, but these solutions did not affect the composition and quality of the alloy. The content of molybdenum salt in the electrolyte is usually 0.015 M Na_2MoO_4, and the perrhenate concentration is 0.0035 M $KReO_4$. Electrolytes operate in a wide pH range (from 3.0 to 0.1), and the cathodic current density usually does not exceed 40 mA cm^{-2}. The electrolyte temperature in the range of 50-75 °C contributed to the production of shiny precipitates. Thus, on the basis of experimental data, for the production of rhenium-molybdenum alloys containing 45-80 wt.% Re, the following electrolyte composition (mol l^{-1}) is recommended: 0.0015 M Na_2MoO_4 + 0.0035 M $KReO_4$ + 2 M H_2SO_4; pH 0.4; scan rate 5 mV s^{-1}; *t* = 75 °C.

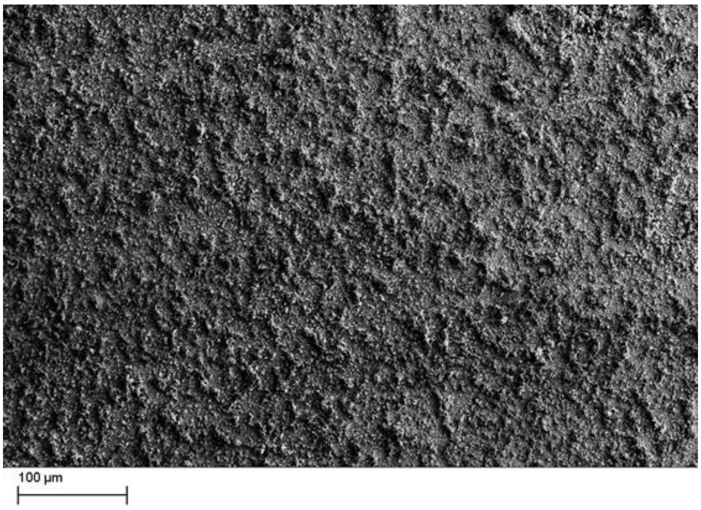

Figure 5. *SEM image of Re-Mo thin film deposited on Pt electrode (production of rhenium-molybdenum alloys containing 45-80 wt.% Re from 0.0015 M Na_2MoO_4 + 0.0035 M $KReO_4$ + 2M H_2SO_4; pH 0.4; t = 75 °C)*

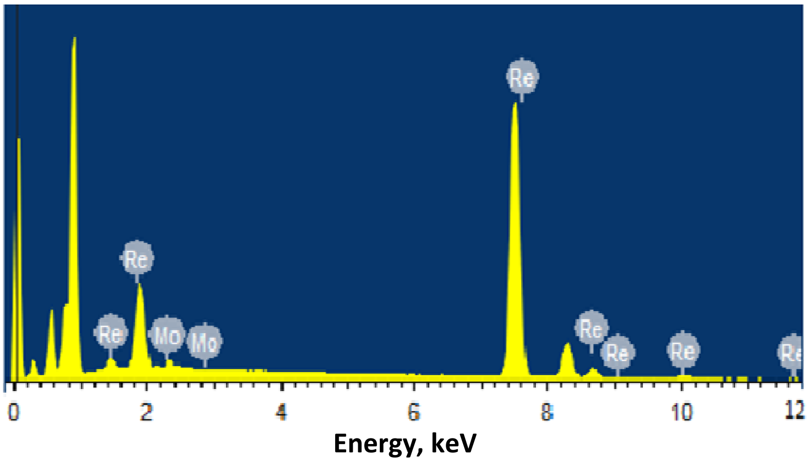

Figure 6. *Elemental analysis of Re-Mo thin film deposited on Pt electrode (production of rhenium-molybdenum alloys containing 45-80 wt.% Re from 0.0015 M Na_2MoO_4 + 0.0035 M $KReO_4$ + 2M H_2SO_4; pH 0.4; t = 75 °C)*

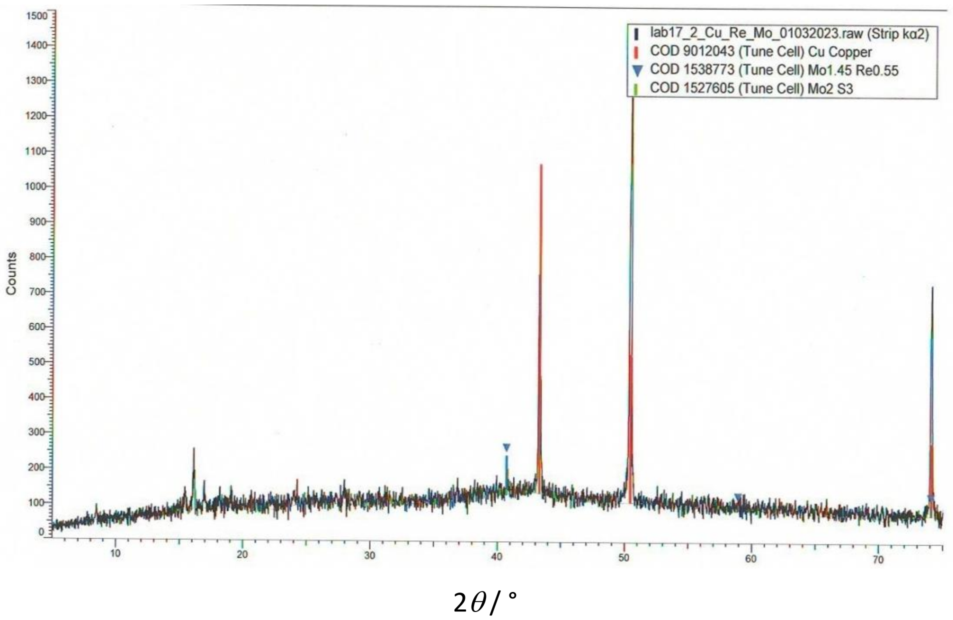

Figure 7*. X-ray pattern of deposited Re-Mo thin film on Pt electrode and annealed at 500 °C for 2 hours (production of rhenium-molybdenum alloys containing 45-80 wt.% Re from 0.0015 M Na_2MoO_4 + 0.0035 M $KReO_4$ + 2 M H_2SO_4; pH 0.4; t = 75 °C)*

Conclusions

1. Based on the study of cyclic voltammograms recorded on Pt electrode during co-electroreduction of rhenium and molybdenum ions from rhenium and molybdate solution in a very acidic electrolyte using sulfuric acid, the conditions of deposition of nanocoatings of Re-Mo alloy system were determined. The influence of various factors on the composition and quality of coatings was studied.

2. The studied factors were concentrations of individual components and total concentration of components in the electrolyte, the temperature of electrolyte, the current density of deposition and concentration of the sulfuric acid solution. It was established that with the increase of rhenium content in the electrolyte and increase of temperature, the rhenium content in deposits becomes higher.

3. In order to obtain alloys of rhenium-molybdenum containing 50-80 at.% Re, the following electrolyte composition has been recommended: 0.0015 M Na_2MoO_4 + 0.0035 M $KReO_4$ + 2 M H_2SO_4, pH 0.4; t= 75 °C.

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