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RESEARCH ARTICLE

ELECTRODEPOSITION OF Re-Cu-Se ALLOYS FROM SULPHUR ACIDIC ELECTROLYTES

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ABSTRACT

The formation of the triple alloys Re-Cu-Se on the platinum electrode at volt amperemetric cycling has been studied. The investigation was carried out from sulphur acidic solution containing selenious acid, potassium perrhenate, chlorine copper. The kinetics of the processes was controlled using the measurements by the method of cyclic volt-amperometry on the device İVİUSTAT. For the analysis od composition and structure the methods of XRD (X-ray diffraction analysis) were used, and the investigation of films' morphology on platinum and copper supports was conducted on scanning electron microscope (SEM). To depict the formation of the systems the corresponding mechanism of electrodeposition was suggested. It is shown that the process proceeds through several stages. The chemical composition of the obtaining layers of thin coatings makes up 14.7 at %Re, 39.6 at %Cu and 14.6 at % Se. The chemical composition of the obtaining films was determined using the method of atomic adsorption spectroscopy (AAS) with application of the spectrometer Perkin-Elmer.

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INTRODUCTION

For many years thin hard phase films of metal' chalcogenides have been the subject of interest, mainly due to their probable application to trasformers of solar energy, solar batteries, photoconductors. sensors, etc. (Andrey Enyashin and Iqor Popov, 2009; Berkh *et al*., 2014; Thomas *et al*., 2004; Naor Adi *et al*., 2010; Salakhova, 2003). Among chalcogenides of metals, rhenium selenides and sulfides are the interesting semi-conductors, which are used in photodetectors and photoresistences. Thin films of selenides and sulfides of rhenium draw attention of the numerous researchers because of cheapness, accessibility and semiconducting properties. The thin coverings of rhenium chalcogenides present the most perspective material for transformers of solar energy. Owing to their unique properties: the high coefficient of adsorption, width of the banned zone providing the possibility of transforming solar light into photocurrent-chalcogeniodes of rhenium may be widely applied to preparation of solar thin film elements. In the past for deposition of thin films of rhenium chalcogenides a series of methods was used. However, the cheapest and technological is the method of electrodeposition. It takes place in one stage, is realized at low temperatures not exceeding 90ºC, has a low cost. At the same time, electrodeposition as a consequence of its electric nature, affords possibility of a precise control of a width of film. It permitted to use different electrochemical systems and methods for successful deposition of the binary alloys of rhenium chalcogenides (Salakhova, 2008; Salakhova and Majidzada, 2011; Salakhova and Aliyev, 2012; Salakhova *et al*., 2014; Salakhova *et al*., 2013; Salakhova, 2014; Salakhova *et al*., 2015; Salakhova *et al*., 2015; Dergacheva and Chaykina, 2008). To the present there are several reports on electrodeposition of the thin films Re=X (X=S, Se and Te). We also studied the process of electrodeposition of thin films Re-X (X=S, Se and Te) from different electrolytes for several years. In work as electrolytes there were applied sulfate, chloride-sulfate, alkali and thioureic solutions containing various concentrations of rhenium and chalcogen (S, Se, Te). It is established that electrochemical formation of thin film of rhenium chalcogenides proceeds through a number of complicated electrochemical processes.

The analysis of the results of measurements of cathodic and anodic polarization curves under the joint electrodeposition of rhenium with chalcogenides shows that the process of the joint deposition is accompanied by depolarization that shows the formation of chemical compound or solid solution on the basis of these compounds, determines a field of potentials at which on a cathode the compounds of stoichiometric composition are formed. We have established that the mechanism of joint electrideposition of rhenium with selenium from sulfate and alkali electrolyte depends on concentration of bivalent selenium formed on a cathode which optimizes reduction of rhenium with the formation of chemical compound $ReSe_2$ {5-8}. At joint deposition of rhenium with tellurium (Salakhova,

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2008; Salakhova and Majidzada, 2011) chemical activity of tellurium plays a basic role, connected with its tendency to the deep reduction, and depolarization of tellurium with rhenium from the acidic electrolyte is connected with change of the nature of tellurium electrode. In work (Salakhova *et al*., 2014) it has been established that joint electrodeposition of rhenium with sulphur from thioureic electrolytes depends on adsorption of colloide sulphur, and both rhenium and sulphur isolate into an alloy with depolarization that testified to the formation of chemical compound $ReSe_2$. However, both the double and triple alloys of the rhenium chalcogenides have the wide fields of application. That is why the scientists in this field are put before the question on working out the methods of obtaining these triple alloys. Simultenous electrodeposition of three components for the purpose of receiving a compound with the given stoichiometric composition is a complex task because the standard potentials of electro reduction of ions differ substantially. To solve it the profound investigation is demanded in the field of electrodeposition of multicomponent semi-conducting materials that enables to create new materials and new structure. The aim of the present work was determining the optimal regimes of electrodeposition of the triple alloys on the basis of rhenium chalcogenides from sulphur acidic electrolytes.

Methods of experiment

As a working electrode was used an electrode with a visible surface 0,07 sm^2. Three-electrode cell contained investigated electrode, subsidiary platinum electrode of 4 sm^2 area and chlorine silver electrode of comparison. All the values of potentials are cited concerning this electrode. The working electrodes were washed with alcohol and water. The ampere-voltaic curves were registered nox mixing. Deposition of the films for investigation of a structure and composition was carried out on Pt, Cu, Ni support of 2.0 cm^2 area. The working temperature at electrodeposition - 75ºC, time of deposition from 30 to 60 min. After deposition the samples were washed with distilled water, pH was determined on the device. The investigation was carried out from sulphur acidic solution, containing selenious acid, potassium perrhenate and chlorine copper. Kinetics of the processes was controlled by means of measurements by the method of voltampermetry on the device IVIUMSTAT. For the analysis of composition and structure the methods of XRD (X-ray diffraction analysis) were used, and the investigation of the films morphology on platinum and copper supports was conducted on scanning electron microscopy (SEM). The X-ray diffraction analysis of obtaining films was made on the plant DRON-5 at C_uK_a –radiations. The films were obtained in galvanostatic regime without mixing electrolyte. For the analysis the cathode sediment was deluted at heating into the concentration HNO_3. The amount of copper was determinated separately by atomic adsorptive spectrophotometer of AAS-IN firm Cari Zeis Zean. The quantity of rhenium was determinated with thiourea.

Experimental part

The mechanism of the process of electrodeposition of the alloys Re-Cu-Se has not been known up to present and working out a theory of the formation of the triple alloys is of great scientific and practical value. In the present work there the data referring to the formation of layers of thin films of Re-Cu-Se on platinum electrode are given. In order to trace the course of the electrochemical reactions in a solution and to choose the field of potentials for deposition of Re-Cu-Se there was applied the method of cyclic voltamperometry. At Fig.1 presented is the typical cyclic voltamperogram (curve 2) taken on the working platinum electrode in $5\cdot10^{-2}$m solution H_2SO_4 containing $CuCl_2$. On voltamperogram there is a narrow anodic peak (peak A) at E_p=0.2V. The cathode wave meets the reduction of Cu^{2+}

$Cu^{2+} + 2e = Cu^o$ (E_o = 0,337V)

An appearance of anodic peak at E_p=0.2V indicates to accessibility of Cu sites on a surface. Afterwards the peak of oxidation, current falls down to zero that shows the end of the process of Cu^o oxidation. When in a solution simultaneously $CuCl_2$ and H_2SeO_3 exist on cathodic and anodic ampere-voltaic curves there appear several cathodic peaks a_1, a_2 (Fig.2, curve 1) on voltamperogram during anodic development there appear corresponding peak A_2 at E_p= +0.43V (Fig.2, curve1). Note that at development in a positive direction the peak of solution Cu^o (Fig.2, curves 1) lack. Thus, one can make a logic suggestion that reduction of H_2SeO_3 proceeds at the same time with electrodeposition of copper. However, on the anode branch volt-ampere curves observed the appearance of additional peaks oxidation typical to triple systems and absent on the volt-ampere curve to double system Cu-Se (Fig.2). Even with the addition of a small concentration of rhenium ions in the solution, an additional peak of oxidation appears at a potential + 0,70V due to the dissolution of the triple compounds. At reverse development of ampere-voltaic curves there are observed two separate peaks of oxidation ions at E_p= +0.43V (peak A_1), the other E=+1.058 (peak A_2) (Fig.2). The peak can be ascribed to oxidation of CuSe in the process of bi-electrode reaction. On cyclic volt-amperogram the peaks of Se oxidation are absent. Thus, it is possible to conclude that copper form sediment transfers into solution (oxidizes) as a result of what Se deviates mechanically:

Anodic peak A_2 meets oxidation of adsorbed compounds of selenium (Dergacheva and Chaykina, 2008; Dukstiene, 2003)

In Fig.3 cited is cyclic voltamperogram of electrode in $5\cdot 10^{-2}$ m solution of H_2SO_4 containing $1\cdot10^{-3}$m.H_2SeO_3 +$5\cdot10^{-3}$m Cu SO_4 + $1\cdot10^{-3}$m $KRe0_4$ For investigation of the joint deposition of three components Cu $_{(II)}$, $Re_{(VII)}$, $Se_{(IV)}$ from sulphur acidic solutions a series of experiments was carried out. Due to increasing concentration of rhenium $Re_{(VII)}$ in the electrolyte the current peak grows. For concentration of Rhenium (VII) in the solution $1\cdot10^{-3}$mol/l and more and one more additional current peak of oxidation appears. The first series was carried out at the constant concentrations of ions of copper $C_{Cu(II)}$= $5\cdot10^{-4}$, selenium $C_{Se(IV)}$= $1\cdot10^{-3}$mol/l^{-1} in consecutive increase in concentration of rhenium ions. The second series was conducted by way of electrodeposition from sulphur acidic electrolytes in which the constant concentration of rhenium ions $C_{Re(VII)}$= $1\cdot10^{-3}$, selenium $C_{Se(IV)}$= $5\cdot10^{-4}$mol/l was kept, and the concentration of copper ions was gradually increased. Ampere-voltaic curves received in the first series of experiments showed that a cathodic branch of ampere-voltaic curve of reducing Cu $_{(II)}$, $Se_{(IV)}$ agrees with the data, described in work. It is found that in the field of potentials from +0,5 to -0.2V the basis process of the joint reduction of copper and selenium leads to the formation of compound $CuSe_x$. At more negative potentials on cathode curve the current peak is, connected with the formation of compound Cu_2Se and isolation of selenium hydrogen.

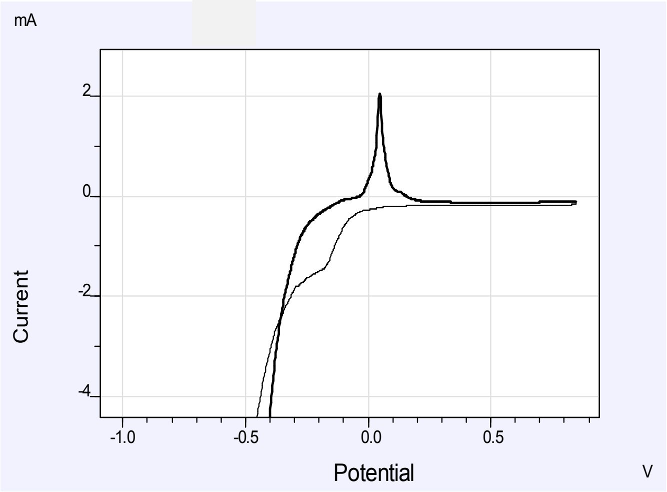

Fig.1. Volt-ampere cyclic polarizing curves of cuprum on the platinum electrode at 4µV/c in the electrolyte contest, mol/l: $6\cdot10^{-4}CuCl_2\cdot2H_2O + 2H_2SO_4$ at t=70°; $V=0,005VS^{-1}$; pH=4

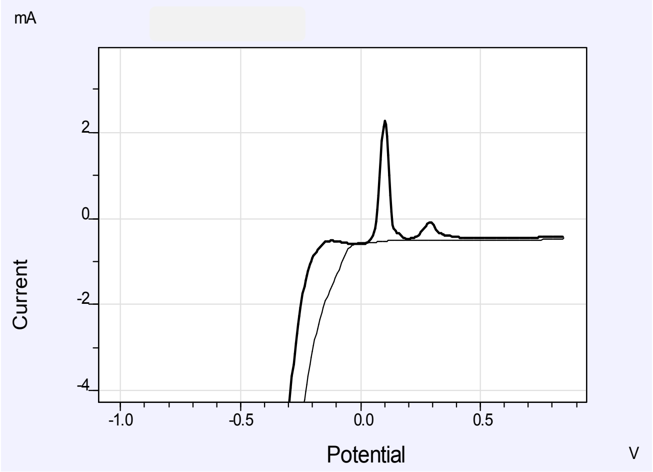

Fig.2. Volt-ampere cyclic polarizing curves of selenium(IV) and cuprum(II) on the platinum electrode at 4µV/c in the electrolyte contest, mol/l: $6\cdot10^{-4}CuCl_2\cdot2H_2O+9\cdot10^{-4}SeO_2 + 2H_2SO_4$ at t=70°; $V=0,005VS^{-1}$; pH=0,38

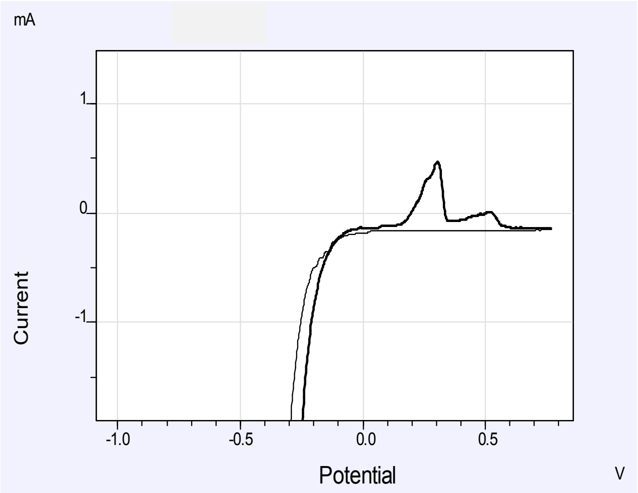

Fig.3. Volt-ampere cyclic polarizing curves of rhenium (VII) on the platinum electrode at 4µV/c in the electrolyte contest, mol/l: $6,9\cdot 10^{-4}KReO_4+2H_2SO_4$ at t=70°; $V=0,005VS^{-1}$; pH=0,1

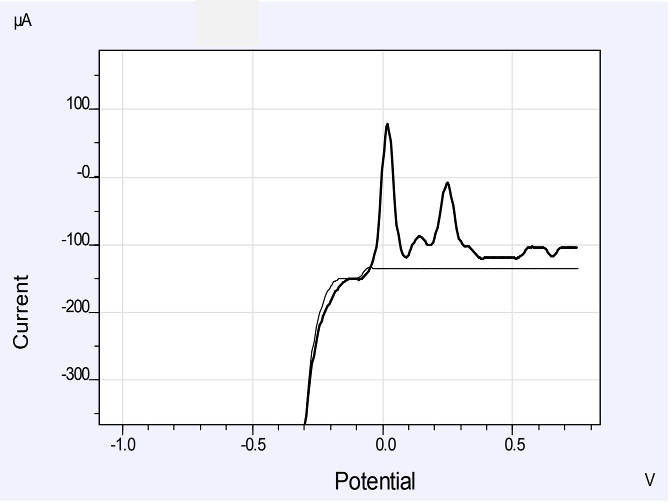

Fig.4. Volt-ampere cyclic polarizing curves of cuprum(III), selenium(IV) and rhenium (VII) on the platinum electrode at 4µV/c in the electrolyte contest, mol/l: $6,9\cdot 10^{-4}KReO_4+9\cdot10^{-4}SeO_2 + 6\cdot10^{-4}CuCl_2\cdot2H_2O + 2H_2SO_4$ at t=70°; $V=0,005VS^{-1}$; pH=0,1

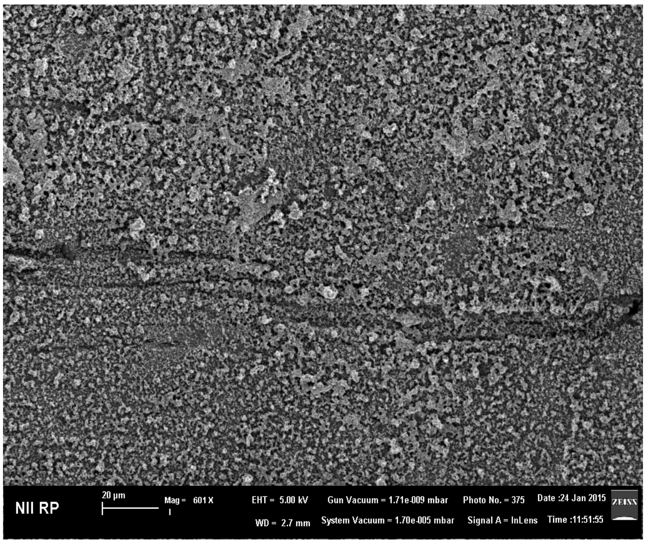

Fig.5. Scanning electron micrograps of electrochemically deposited Re-Cu-Se films on platinium

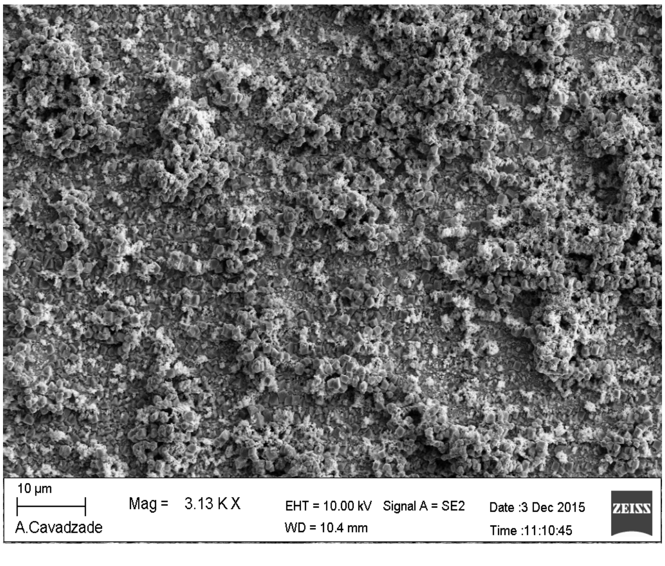

Fig.6. Scanning electron micrograps of electrochemically deposited Re-Cu-Se films on copper

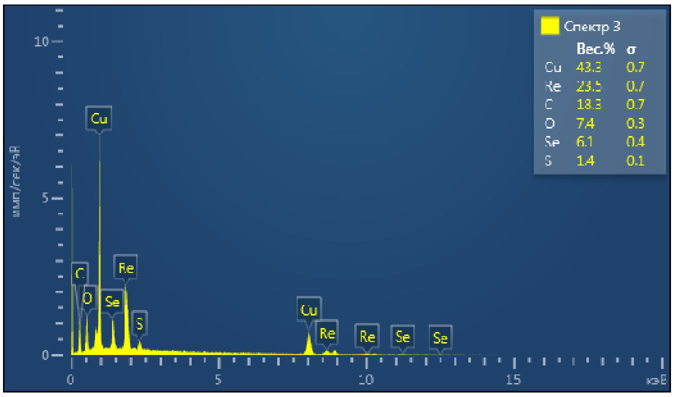

Fig.7. SEM and EDAX analysis of the front side Re-Cu-Se film obrained by electrodeposition

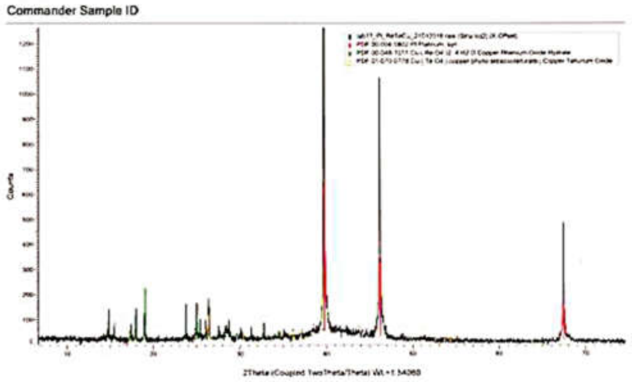

Fig.8. XRD patterns of the electrodeposides Re-Cu-Se film platinum subsrate

On anodic branch of ampere-voltaic curve the current peak at E_{ia} = 0.25V is conditioned by oxidation of copper ions from two-component compound Cu_2Se

Current peak at E_{2a}= 1.1V corresponds to oxidation of elementary selenium, formed on electrode to Se (IV).

As it is known the rhenium stays in sulphate electrolytes in the form of ReO_4^- and its reduction consists of several separate processes.

$ReO_4^- + 8H^+ + 7e \rightarrow Re + 4H_2O$

According to the work (Salakhova *et al.*, 2014) the degree of ReO_4^- -ions goes stage-by-stage and each stage of formation the intermediate products is characterized by a certain electrode potential, which becomes more negative in the process of rehabilitation, which can also provide the approach of Re and Se potentials settlement.

$ReO_4^- + 2H^+ + e \rightarrow ReO_3 + H_2O$; $E_1 = +0,77V$
$ReO_3 + 2H^+ + 2e \rightarrow ReO_2 + H_2O$; $E_2 = +0,4V$
$ReO_2 + 4H^+ + 4e \rightarrow Re + 2H_2O$; = +0,26V

Thus, the rhenium reduction in strong acid electrolytes goes according to the stage, through the formation of intermediate oxides film, about which tell us red and blue sediments in the obtained film. In order to have a whole information about the joint electrodeposition of Re with Se, there were measured the cycling polar curves of rhenium in sulfate electrolyte at the different involutions. There are two sharp waves on the curve of a cathode halfcycle. One of them is at the potential 0,2 - 0,3 V, the other – at(-0,3)-(0,4)V (s.c.e). Formation of these waves can be explained by the step mechanism of reduction the perrenate ions. The character of anode half cycle also proves this suggestion. The anode wave forming at the potential 0,1-0,2V (s.c.e.) can be explained by Re dissolving, and distinctly expressed peaks – to dissolving of ReO_3 and ReO_2 correspondingly. The current peak of oxidation at +0,45V is not typical for double systems Re-Se and Cu-Se and appears only with joint deposition Se(IV), Re(VII) and Cu(II)in the terms of large excess rhenium ions (fig.4) This peak may be associated with oxidation of rhenium from triple compounds $ReCuSe - 7e \cup Re^{7+} + CuSe$ Comparison of voltampere curves of double system (Fig.3) allows to make conclusion, that current peak at E= +0,25V caused of oxidation copper from double compound Cu-Se. At addition and subsequent increase in the concentration of Re ions in electrolyte a cathodic branch of ampere-voltaic curve does not change practically. The wave of reducing Re(VII) of own lacks. In the work there has been carried out the investigation of influence on a value of currents of cathodic and anodic peaks of concentration of rhenium ions in the $2{,}5\cdot10^{-3}$ $mol\cdot l^{-1}$ range at maintenance of the constant concentration of copper and selenium ions in electrolyte. Increasing concentration of Re (VII) ions leads to increasing oxidation current of Se(0) that testifies to additional accumulation of selenium on the account of decomposition of the compounds formed on electrode. As well there is observed the increase in current of anodic peak of oxidation of triple compound. The current of oxidizing double compound Cu_2Se_2 decreases and in future remains constant at changing the concentration of indium from $5\cdot10^{-4}$ till $2\cdot10^{-3}$ $mol\cdot l^{-1}$. In the given range of concentration an increase in current of triple compound oxidation. The current peak conditioned by oxidation of the compound $ReSe_2$ remains slight and depends weakly on the concentration of rhenium (VII) ions. The change of the concentration of rhenium ions in practice does not influence on the potentials of cathodic processes peaks. The cathode current connected with reduction of Se^{-2} ions, abruptly falls at the concentration of rhenium ions $5\cdot10^{-4}$ $mol\cdot l^{-1}$ and then gradually decreases.

At the joint co-deposition of three components for the purpose of obtaining the sediments of the compound Re-Cu-Se the choice of electrolyte composition was based on the data of two above depicted series of experiments. The main task consisted of the choice of ration of concentration and potential of deposition at which the priority would be the process of deposition triple compound Re-Cu-Se, at the same time the process of deposition on electrode of binary phases of copper-selenium and rhenium won't be long. From the obtained voltamperic curves (4) it is established that peaks of triple compound oxidation at the potentials – 0.37 and +0.72V re more intensively displayed at Cu : Re : Se = 1:2:2 ratio of concentrations in electrolyte. At deviation from this ratio these takes place the increase of oxidation peaks corresponding to the binary compounds copper-selenium rhenium-selenium, slight deviation from the indicated ration towards surplus of copper (II) ions or selenium (IV) in solution, deposition of surplus quantity of copper (0) or selenium (0) takes place. At selected ratios of the concentration of the components in electrolyte the potential potentiostatic deposition of the ternary compound film on the platinum and copper electrodes of 2 cm^2 area at temperature 75ºC within one hour. After electrodeposition the samples were washed with distilled water, and annealed for 10 minutes on air at temperature 410 ºC. The phase composition of the received films was determined by RPhA on diffractometer. Thus, electrodeposition from electrolytes containing ions of rhenium (VII), copper (II) and selenium (IV) on the background of 2 mol/l sulphuric acid in chosen conditions of electrolysis and annealing permits to obtain the thin coatings Re-Cu-Se. On the basis of data described in the present article the preliminary model of the mechanism of electrodeposition of thin coatings Re-Cu-Se was suggested. Here, we can note three basic research electrochemical stages:

The first stage –	absorption and reduction of the selenium particles on a surface of the platinum electrode.
The second stage –	adsorption between Cu^{2+}ions with adsorbed compounds of selenium with intermediate degree of oxidation.
The third stage -	the formation of the alloy Re-Cu-Se. Ions of Cu^{2+} and Se^{4+}reacting with rhenium ions forms the thin films of Re-Cu-Se.

It is interesting to note that the formation of the thin coverings Re-Cu-Se appears in the presence of clearly expressed peak observed in the same field of the potentials (peak C_5). As well it is clear that this peak meets rather complicated process. Several reactions proceeding in parallel meet this peak. The latter reacts with ions with ions, but this process requires more detailed investigation that will be the subject of our further work. To understand the nature of some phenomena in this article, the additional investigations are demanded. The analysis of the corresponding electrochemical mechanism presents a particular interest both for theoretical and applied works. It is in particular important to learn to control morphology and stoichiometry of electric sediments of the alloy Re-Cu-Se. XRD diagram of the thin coverings Re-Cu-Se has not been analyzed in detail as in literature the data for comparison lack. In Fig.5 the data on morphology of the alloy Re-Cu-Se registered on the device SEM are presented. It was established that on the platinum cathode the nano particles of the alloy Re-Cu-Se are grown that have the certain law-regulating structure resembling the little islands. They have a form of a circle and ellipsis what is connected with that the process of electrodeposition runs unstable. That is, during the process the influence of parameters which lead to oxidizing a surface, is of great importance. At examination of the samples on platinum there are clearly seen different phases on a boundary of deposited and non-deposited particles. It is established that the islands of nanoparticles have a value in the range 80-350 nm. The triple alloys were also obtained on copper support. In Fig.6 the data on influence of the material of electrode on structure of deposited alloy, are presented. As is seen from Fig.6 the samples got on copper support very strongly differ from those on platinum support. As well, it should be noted that the sizes of deposited substances many times lesser than those of copper and make up 50-120nm. In Fig.7 the chemical analysis of the samples data is presented and the present content of these elements are given. According to RPhA data and obtained films in this way besides the compound Re-Cu-Se some quantity of the double-phase Re-Se existed (Fig.8).

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Conclusion

1. On the basis of investigating volt ampere dependences at the joint electrodeposition of ions of perrhenate (VII), selenium (IV) and copper (II) from sulphur acidic electrolytes on Cu (copper) electrode the conditions of potentiostatic deposition of the thin triple coverings Re-Cu-Se have been established.
2. By the method RPhA and investigation of morphology of the films on copper support and atomic adsorption spectroscopy (AAS) method of analysis, the composition of the obtained triple covering Re-Cu-Se has been confirmed and surface morphology has been studied.

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