The Electrochemical Deposition of Rhenium Chalcogenides from Different Electrolytes

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Electrodeposition Rhenium Alloys, Azerbaijan

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Abstract: In this article were generalized publications for 20-30 years. The properties of the modern electrochemical methods for obtaining rhenium and its alloys had been given. More than 100 scientific works for rhenium obtaining and its alloys were analyzed. In the reviewed article has been shown that rhenium more often deposited from sulfate, phosphoric acid, ammonium sulphate, citrate, alkaline and other electrolytes. The property of electrodeposition rhenium with metals (Ni, Co, Fe, Zn, Cr, Pt, Pd, Rh, Au, Ag, Cu, Se, S, Te and so on) has been shown. The electrolyte composition and terms regime of electrolysis for obtaining these alloys rhenium from different electrolytes had been given. With using potentiostatic, voltamperic, temperature and kinetic methods was estimated kinetic and mechanism of mutual electrodeposition rhenium with different metals. In the review were estimated scientific base of regularity for mutual electrodeposition rhenium with chalcogenides from different electrolytes and synthesized new semi-conductive covers of rhenium chalcogenides by using different electrochemical ways. As electrolute were used sulphate, teasulphate, chloride sulphate, chloride borate, alkaline liquids, containing different concentrations of rhenium and chalcogenides (S, Se, Te). Analysis of results for measures cathodic and anodic polarization curves for mutual electrodeposition rhenium with chalcogenides (S, Se, Te) has been shown, that the process accompanied depolarization, which proves the formation of a chemical compound or solid solution on the base these compounds and estimates potential areas for which on the cathode obtain compounds stoichiometric composition. In the review the works concern electrodeposition triple alloys of rhenium with different metals were given. All chalcogenodes rhenium are semi-conductive materials as has been estimated.

Key words: Electrochemistry, thin films, rhenium chalcogenides, rhenium alloys.

1. Introduction

The authors of present work concentrated their efforts on rhenium and its alloys. This metal has some specific properties and finds its application in various fields of semi-conducting industry. In recent years a sphere of using these compounds was substantially widened space technique, electronics, IT sector and so on. There was also emerged a necessity to investigate their physical and chemical properties and to elaborate effective technology of getting alloys basing on these elements. There are some works and patents describing methods of obtaining rhenium shining metallic sediments cited in the references [1-40].

Substantial mechanical strength, hardness, high electrical impedance and other properties of rhenium alloy rhenium and its alloys to be widely used in various fields of technique. Alloys of rhenium with a range of metals are used in electronic, electrometrical and atomic technique as well for production of special coatings [1-9].

There are various methods for obtaining thin films of rhenium semi-conducting alloys. But the analysis of known methods of obtaining rhenium chalcogenides’ thin films showed that the most perspective and less expensive is electrochemical method which has those advantages, that it does not need sophisticated equipment, high temperatures and allows to produce an alloy of high purity. Using this method it is easy to control thickness, a composition of a coating, and, varying electrolysis regime, to get
coatings with demanded composition[14, 15] The purpose of this paper is to summarize, organize and view publications for 20-30 years and to identify trends and opportunities of modern electrochemical methods (voltammetry, potentiometry, ammeter, etc.) for producing rhenium alloys. The survey provided more than 100 works devoted to the preparation of rhenium alloys by electrochemical method. Review article also includes the new works on electrodeposition of chalcogenide rhenium by the electrochemical method from different electrolytes.

The present work was made aiming to research the appropriate processes, to determine scientific base of electro-deposition of rhenium chalcogenides and to define physicochemical properties of produced thin films. The electrodeposition of metals is one of the main sections of electrochemistry having great practical importance. Sphere of application of electrolytic metals constantly widens due to rapid growth of technique. Nowadays it is hard to name a field where electrolytic metals and alloys are not presented.

2. Electrodeposition of Rhenium and Its Alloys

The electrodeposition of metals is carried out both from water solutions and non-water organic and melts environments. Main regularities of electrodeposition of metals from water and organic environment do not differ substantially. But it is possible to deposit from melted environment those metals which do not separate from water solutions (vanadium, molybdenum, tungsten, zirconium and other). Metallic rhenium and it’s alloys have unique physico-chemical properties, due to winch find wide application in the most important fields of modern technique [1-10]. Rhenium alloys with metals of platinum group can be used for production of electric contacts having high operational properties. Distinctive property of rhenium is its resistance to electro-corrosion that prevents burning of contacts.

Further is opening a new field for application of rhenium-oil refining industry, in which rhenium in combination with platinum is used as catalyst in oil reforming processes for production of high octane benzenes. The application of rhenium-platinum catalysts prolongs a life period of catalyst five times and raises the process effectiveness more than by 60%. Simultaneously the octane number of produced benzene rose to 100-105 units. Thus the application of catalysts of mentioned type provided a new quality jump in oil refinery. Thin coatings of rhenium disulphide were offered as catalyst for alcohols dehydrogenization process. Mostly interested are new reports about works in the field of application of rhenium and its alloys for needs of air- and rocket industry. Not less interesting and important may be considered the application of rhenium in nuclear technique [7, 11]. The rising consumption of rhenium stimulates a searching of new sources of raw, effective methods of its refining, development of new methods of production of rhenium and its alloys.

Hot sulfuric acid reacts with rhenium, transforming it to HReO₄. Rather easily rhenium dilutes in bromine water at slight heating. Rhenium vigorously reacts with halogens. It forms simple and complex halogenides and oxyhalogenides. Rhenium halogenides present interest for technologies and analytical chemistry, because they are volatile. The purification of metallic rhenium from impurities by the method of rhenium purification after its chlorination is based mostly on volatility of rhenium chlorides.

Rhenium reacts with sulphur, selenium, tellurium and forms sulfides, selenides and tellurides [2]. With selenium rhenium forms following compounds: Re₂Se₇, ReSe₂, ReSe, Re₃Se₂. In rhenium-sulfur system there was defined occurring of rhenium sulfides ReS, Re₂S₂, ReS₂, Re₂S₅, ReS₅. Rhenium sulfides and selenides are effective catalysts for hydration of organic materials. Their advantages in comparison with metallic catalysts of platinum group
consist of that they are not poisoned by sulfur containing compounds. Rhenium sulfides also catalyze redox reactions of NO and N₂O at the temperature of 100 °C. Besides mentioned fields of application rhenium can be used in analytical chemistry (as a reagent for potassium, for fractured crystallization of rare earth metals as it is generally known [3-10], rhenium is deposited from sulfuric, ammonium-sulfuric, phosphatic, oxalic, citric, alkaline and other electrolytes. The investigation of the process of electrodeposition of rhenium, one of trace chemical elements, has practical and theoretical interest [1-5, 8-10, 21].

The group of Chilian scientists studied rhenium and rhenium oxides being obtained by electrodeposition from alkaline perrhenate electrolyte in a standard electrochemical cell (cathode and anode). The Cu substrate was used as the cathode, with an apparent surface area of 13 mm², whereas the Pt electrode was the anode, with an apparent surface area of 1 cm². The galvanostatic electrodeposition was conducted with a 5 A-30 V GW rectifier (model GPC-3030D), which also allowed cell voltage measurement. Regarding rhenium and rhenium oxide electrodeposition was related to the use of an aqueous acidic electrolyte (NH₄ReO₄ or HReO₄ dissolved in H₂SO₄) and in some cases preparing and electrolyte by dissolving metallic Re in hydrogen peroxide. The authors found that on the zone near the edge of the dendrite of the electrodeposited material, it is possible to ascertain that the mechanism of electro crystallization involves the reduction of Re (7+) from the ReO₄⁻ ions to metallic Re (0) throughout the successive reduction of ReO₃ (6+) to ReO₂ (4+). It is possible to electrodeposit rhenium rhenium and rhenium oxides from alkaline aqueous electrolyte without evident formation of powdery deposits [24].

In the works [25, 26] there were synthesized and studied electrochemical and photophysical properties of a thin coating of Rhenium.

In the monograph [27] the methods of extraction of rhenium from raw and secondary materials, obtaining metallic rhenium and products from it are described. Special attention was paid to extraction-sorption processes, having dominating position in rhenium metallurgy. Specific examples of existing technological schemes of rhenium extraction from various kinds of materials and their equipment design [27] are given.

In Uruguay the comparative study of electrochemical and optical properties of rhenium deposited on gold and platinum was carried out [28]. Rhenium-containing films were grown on gold and platinum after different potentiostatic and potentiodynamic polarizations in the 0.20 V to 0.70 V range (vs rhe) in aqueous acid perrhenate.

The method [29] involves placing the stent in a series of rinsing and electroplating solutions, one containing radioactive rhenium (186Re, 188Re, or both).The overall processing time is 15 min and the procedure may be conveniently applied just prior to the stent insertion. The plated stent contains radioactive rhenium in a 1.2 microm-thick cobalt layer, with an outer 2 microm layer of gold.

Electrochemical oxidation of silver and rhenium electrodes in molten LiF-NaF-KF eutectic at 600 °C was investigated by cyclic and convolutional voltammetry [30].

Yakovlev M.A. [31] studied modeling and optimization of the processes of extraction of rhenium from multi-component alloys. It was defined that when anodic dissolving alloys on the base of nickel, rhenium, nickel, cobalt, aluminum and chrome practically fully go into solution, tungsten and molybdenum go as tungsten and molybdenum acids and tantalum and niobium go to sludge.

L.G. Holz [32] in the PH.D thesis named “The voltammetric determination of rhenium in raw and anthropogenic materials” for the first time determined and interpreted peaks, observed on anodic and cathodic voltammetric curves in the processes of
The Electrochemical Deposition of Rhenium Chalcogenides from Different Electrolytes

According to the literature data [37], for obtaining rhenium coatings the electrolytes containing fluoride estimated to be more preferred compared with a sulfate electrolytes. From these electrolytes rhenium coatings on electrodes of copper, molybdenum, and stainless steel may be deposited.

The authors [38] investigated the processes of electrolytic production of rhenium coatings from the electrolyte KCl-NaCl-ReCl₄ with a current density 5-200 mA/cm² at 680-970 °C. At this process the dense coating of rhenium is forming, having thickness 20-40 microns and length up to 10 m. The diffusion coefficient of Re⁴⁺ ion at 790 °C is 2.8 × 10⁻⁵, at 840 °C-3.5 × 10⁻⁵ cm²/sec.

The process of rhenium electrodeposition was investigated by the method of measurements of charging curves, measurements of overloading of rhenium discharging and hydrogen on it, as well as by defining a structure of sediment (by X-ray and electron-microscopic methods). The authors [10, 11] made a conclusion that in the process of electrodeposition rhenium is saturating by hydrogen (14-22 atomic%), main part of which is discharging at room temperature and only 0.5 at % at > 500 °C. The author [10] supposed a physical and chemical sorption of hydrogen with formation of intrusion phases thru ReH hydride. The electrodeposited metallic rhenium has thin-dispersed structure and high tension (to 1,500 kg/cm²). There are known alloys of rhenium with many elements, obtaining mainly by thermic method. Alloys of rhenium with tungsten, molybdenum, chrome, nickel and some others have a range of valuable properties: high melting temperature, high specific impedance, low volatility, heat fastness and others. The valuable properties of rhenium alloys allow applying them in most critical parts of various equipment as well as for coating of electric contacts and other parts, working in hard conditions [20, 21]. In connection with this the electrolytic production of some rhenium alloys is a question of a great interest. The works [20, 21, 41-76] were let in on the processes.
of electrodeposition of rhenium together with other metals on solid cathodes. Meyer A. [77] showed probability of electrodeposition of alloys of rhenium with a number of metals (Ni, Co, Fe, Zn, Cr, Pd, Rh, Ag, Au) on platinum cathode. In such conditions a discharging of hydrogen is lowering to 80%. The sediments have good quality.

From one side, a rising of alloy may be explained by rising of hydrogen discharge overstress at alloy comparing with discharge it at rhenium [48]. From other side resulting to alloy formation the enthalpy ($\Delta H^0$) and free energy ($\Delta G^0$) change which obviously have negative values.

A probability of joint electrodeposition of rhenium and metals of ferric group were shown in works [1, 48, 49].

A special attention is to be paid to the works of L.M. Netherton and M.L. Holt [76] in which was shown probability of obtaining alloys Re-Ni and Re-Co with various content of components depending of rhenium concentration in electrolyte with high output by current. They proposed two kinds of electrolytes having following compositions: 225 g/L NiSO$_4$·7H$_2$O, 45 g/L NiCl$_2$·6H$_2$O, 1 g/L KReO$_4$, 30 g/L H$_3$BO$_3$, to second solution was added also citric acid in amount of 70 g/L. From electrolyte with first composition (Ph = 4.6) irrespective of current density an alloy was deposited with high output by current (96-100%) and with low content of rhenium. From second electrolyte (Ph = 2.6), on the contrary, content of rhenium in alloy achieved 60%, but output by current was $\leq$ 50%.

Alloy Re-Ni with 85-90% of rhenium also deposits from electrolyte proposed in [21]. The electrolyte contains 15 g/L KReO$_4$, 5 g/L NiSO$_4$, 50 g/L (NH$_4$)$_2$SO$_4$ and has pH = 2.5-3.0. At temperature 70 °C and current density 2-4 A/dm$^2$ a coating deposits with output by current ~90%. The alloy Re-Ni in this electrolyte can be deposited only under certain combination of pH and current density. In the work [21] successfully was obtained the alloy Re-Ni (85-90% of rhenium) with output by current 90% in the electrolyte containing: KReO$_4$-15 g/L; NiSO$_4$·7H$_2$O-5 g/L; (NH$_4$)$_2$SO$_4$-50 g/L, under pH = 2.5-3.0, current density 2-4 A/dm$^2$ and temperature 70 °C with in dissolvable anodes. High output by current connected with rise of overloading of hydrogen due to co-deposition of nickel.

Were used ammonium-sulfate electrolytes having various compositions [49, 68, 77]. Was defined influence of current density, temperature, concentration of rhenium and metal of ferrous group to the process of electrodeposition two-component alloys Re-Fe, Re-Ni, Re-Co. Was shown that a rise of current density within the limits 2-20 A/dm (50 °C) leads to rise of rhenium content in alloy. The electrodeposition of alloys under optimal current density (5 A/dm) promotes obtaining of shiny coatings with output of current 100%. Particularities of Re-Ni cathodic electrodeposition process were in details highlighted in the works [48, 49]. The authors highlighted that the mechanism of electrochemical discharge of rhenium from perrhenate anion especially with other metals is not clear, that impedes development of optimal technological regimes. The process of forming an alloy by the method of polarization curves measurements was investigated, chemical and phase composition of the alloy was defined, output of alloy by current was calculated. The authors came to the decision that nickel is discharging with substantial depolarization in comparison with separate discharging of metals. For rhenium discharge also mitigates and the depolarization is 20-200 mV.

When investigating a possibility of obtaining of triple alloy rhenium-nickel-chrome were used electrolytes for obtaining of double alloys rhenium-nickel, rhenium-chrome [11]. The obtaining of triple alloy rhenium-nickel-chrome was proceeded by group of Russian scientists [9].

During the investigation electrolytes for obtaining defined double alloy were prepared and was added a salt of appropriate third component. As a result of series of experiments was defined that shiny coatings
of triple alloys are obtaining only in chrome-rhenium bath in which was added nickel sulfate. The quality alloys coatings containing: rhenium-0.5%; nickel-0.28%; chrome-4.5% were obtained from the bath of following composition (g/L): KReO$_4$-50, (NH$_4$)$_2$SO$_4$-40, H$_2$SO$_4$-75, CrO$_3$-15, NiSO$_4$-45.

For electrodeposition of alloys Re-W the authors Sominskaya Z.M. and others [9, 43] recommended solutions on the base of perrhenate and tungsten with addition of H$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$. As a complexion agent which ties tungsten to soluble complex they added citric acid. Alloy Re-W in a form of solid coating or powder separates from solution containing potassium perrhenate and ammonium (6-60 g/L of rhenium), sodium tungstate (3-32 g/L of tungsten) ammonium sulfate (50-200 g/L and citric acid (100 g/L). Maximal output by current as in acidic so in alkaline conditions is 10% and content of tungsten in alloy is 3%. The alloy with maximal concentration of tungsten (10%) was deposited with output by current ~1%.

Were also obtained alloys rhenium-copper with various composition [9, 11]. A dense coating of Re-Cu alloy containing 50% of copper is possible to obtain in concentrated by rhenium electrolyte with composition: 50 g/L KReO$_4$ + 75 g/L H$_2$SO$_4$ + 40 g/L (NH$_4$)$_2$SO$_4$ + 1 g/L CuSO$_4$. At the current density 100 A/dm$^2$ and temperature 75 °C were obtained coatings containing 36% copper. Alloys Re-Cu containing 2.4-3.0% of rhenium were extracted from electrolyte with composition: CuSO$_4$-125 g/L; H$_2$SO$_4$-45 g/L; NaReO$_4$ 200 g/L at temperature 75 °C and current density 1-2 A/dm$^2$.

To get the alloy Re with Cu authors [50] used sulphate electrolyte. The gold and titanium electrodes were used as cathode. Were studied rentgen graphic, electron microscope and X-ray diffraction analyses (EDX, XRD, SEM [50].

The authors of work [51] investigated the mechanism of co-electrodeposition rhenium-nickel alloy on copper backing from bath containing citric acid.

For obtaining of coatings Re-Ir-Ni [52] a deposition was carried out from various aquatic solutions on copper backings with three electrodes by galvanostatic method. The bath contained of iridium chloride, ammonium perrhenate, nickel sulphamate and citric acid.

The alloys of rhenium with nickel also had got the authors of work [53]. For it was used three-electrode cell, the polarization curves were measured in galvanostatic conditions. The electrolyte had in composition ammonium perrhenate, nickel sulphate and citric acid. Was studied a mechanism for nickel-rhenium alloys.

The authors of present work [54] were obtained rhenium alloys with iron group (Me = Ni, Fe and Co). The electrolyte had composition as follows: ammonium perrhenate, nickel or cobalt sulphamate, iron sulphate and citric acid and magnesium sulphamate.

In their previous works authors reported about co-electrodeposition of rhenium and metals of iron group. In the present work [55] the authors in more details investigated a mechanism of co-electrodeposition.

Rhenium also was produced from secondary materials containing rhenium and superalloy of nickel clearly highlighted in work [56]. Were investigated at constant potential electrolyse thin coatings Cu$^{II}$Re at electrolytic reduction CO$_2$. The reduction products were analyzed by FTIR and gas chromatography-mass spectrometry. Were also studied out triple alloys on indium-tin oxide coated by glass substrates from acidic peroxy-polymolybdo-perrhenate solution.

Triple alloy Ni-Co-Re was investigated in alkaline environment and their kinetic parameters were determined. The authors [60] in this study gave data on the production and use of rhenium and its alloys.

Rhenium-nickel alloy was also obtained by authors [61]. Was investigated an influence of temperature, current density, composition of electrolyte on alloy composition. The electrolyte has the composition as
follows: ammonium perrhenate, nickel sulfate and citric acid. For it was used electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence (XRF).

A magnetic material based on cobalt-nickel-rhenium-tungsten-phosphorus (Co-Ni-Re-W-P) composition has been developed by electrochemical deposition [62]. With proper control of process conditions, hard magnetic films with high out-of-plane remanent magnetization (Mr) of 3.11 kG and coercivity (Hc) of 2.33 kOe are achieved. Fabrication of Co-Ni-Re-W-P in the form of microcylindrical arrays of ~50 µm diameter and 90 µm height enhances the vertical anisotropy to a vertical Mr of 5.15 kG and Hc of 2.02 kOe. The materials and fabrication technique of microstructures as reported could be applied for the fabrication technique of microstructures as reported could be applied for the fabrication of magnetic microelectromechanical systems. [62] The authors [63] prepared from aqueous solutions with citric acid as complex forming agent on a surface of Cu-substrate coatings Ni-Re-P (Re = Ce, Nd). At 385 °C with the amount of rhenium 30% (weight %) were obtained amorphous coatings. Rhenium films with various amount of copper were obtained. Qualitative deposits Re-Cu (50%) were obtained from concentrated solutions of rhenium: 50 g/L KReO₄ + 75 g/L H₂SO₄ + 40 g/L (NH₄)₂SO₄ + 1 g/L CuSO₄. At 75 °C, 100 A/dm² were obtained films with 36% Cu. From the solution CuSO₄ -125 g/L, H₂SO₄-45 g/L, NaReO₄-20 g/L at 1-2 A/dm² were obtained films with concentration of rhenium 2.4-3% Re.

For the obtaining rhenium-copper film was proposed the electrolyte CuSO₄ + NH₄ReO₄ [64]. At the potentiostatic mode were obtained foils rhenium-molybdenum and rhenium-tungsten coatings [65]. The composition is 96% of H₂SO₄, potential-5-6 V, current density-60-70 mA/sm².

The work [66] was dedicated to investigation of some electro-physical properties of thin electrolytic films of rhenium chalcogenides, as dynamic and static voltammetric characteristics (VAC). Authors investigated a typical VAC of diode structure measured in static regime and found that diode structure has polar-dependent switching effect. In electrolytic layers of Pt-ReXe₂-Al₂O₃ type, this effect occurs right after supplying of voltage on diode structure. The diode structure showed properties of bi-stable switching. Were also investigated dynamical characteristics of diode structure Me-Re-Xe₂. The investigation of VAC in dynamical regime has great interest for interpretation of phenomena forming the switching effects. Data obtained in present work showed that the structure based at thin films of rhenium chalcogenides, has VAC with S- and N-shaped sectors of negative impedance (NI) both for direct and reverse current direction. In contrast of other devices with NI the elements basing on mentioned alloy have simple production technology and can work at wide range of temperatures. This property let us suggest that devices basing on thin films of rhenium chalcogenides may find wide using in various devices in telemechanics, automation computing technique.

At the conference which has been held in the Moscow 2013 our work “The electrophysical properties of thin films of rhenium chalcogenides obtained by electrochemical method” was presented. Our results found confirmation in the works by L. Agapova and V. Guro [67-68].

3. Methods for obtaining alloys in system Re-X (X = S, Se, Te)

The obtaining of chalcogenides can be performed by various methods, defined by physics-chemical particularities of synthesized compounds and initial matters.

For obtaining of chalcogenides are used various methods: (a) direct synthesis from elements by alloying; (b) absorption from gaseous phase; (c) obtaining of chalcogenides from salts solutions; (d)
The Electrochemical Deposition of Rhenium Chalcogenides from Different Electrolytes

electrochemical method [69-75]. Practically are using all abovementioned methods. In the works [76-84] widely were studied the system Re-X (X = S, Se, Te).

Rhenium forms with tellurium compounds having various compositions of tellurides (Re-Te). In the system Re-Te are known following tellurides: Re₂Te₅, ReTe, Re₃Te₂, Re₂Te₅, Re₂Te₇. A synthesis and investigation of rhenium tellurides was begun comparatively of late. A formation of rhenium tellurides in binary system Re-Te is shown in [80]. A diagram of conditions in this system was made basing the data of thermic analysis, and there are three compounds in system Re-Te: Re₂Te₅, Re₃Te₅, Re₂Te₇. Most tellurized compound in system is ditelluride Re₂Te₅ (42.15% mass. of rhenium), the melting temperature of which is 965 °C. Crystal lattice of the rhenium ditelluride is rhombic and the parameters of the lattice are following: a = 12.987 ± 0.007 Å; b = 13.055 ± 0.008 Å; c = 14.271 ± 0.008 Å.

The system Re-Te was investigated also by authors [78] and according the data of thermic and X-ray phase analysis was drawn a diagram of a condition of this system. In difference with of the work [80] here an interaction of rhenium and tellurium was investigated in whole interval of concentration.

The authors [80] pointed out bad reproducibility of experiments results and supposed that Re₂Te₂ exists within the limits of Re₂Te₂.04 to Re₂Te₂.47. Rhenium ditelluride is a dark gray powder, continually resistant to air and soluble in hot sulfuric acid.

S. Furusev and A. Krekzsus [84] prepared rhenium ditelluride by heating of weighted stoichiometric amounts of components in evacuated and sealed quartz ampoule during twenty days at the temperature 700 °C. After dispersing the samples were annealed in the interval of temperatures 500-1100 °C and then cooled in icy water. The authors made a supposition that crystal lattice of rhenium ditelluride is rhombic.

Rhenium tellurides were also obtained by action of Te and H₂Te vapors in hydrogen flow to powdered Re and ammonium perrhenate using technologies [6, 80]. As a result were obtained dark grey powders with increased content of tellurium. Very bad reproducibility of experiments is to be mentioned. Samples containing 68.35% of Te are two-phased and consist of Re₂Te₂+Te. Despite of all efforts the authors could not get samples exactly corresponding to Re₂Te₂.

Thus, rhenium telluride are unstable even at comparatively low temperatures, together with excess of hydrogen, being deoxidant, causes bad reproducibility of experiments as well as unsuccessful efforts to obtain a compound with the composition Re₂Te₂. Abovementioned shows that using these methods only solid samples or powders of rhenium telluride can be obtained. Was investigated a structure of crystals of Re₂Te₅ grown by gas transporting reaction. The parameters of rhombic lattice Re₂Te₅ were close to ones found in [84] for the compound Re₂Te₂ what is an additional confirmation of possible wide range of homogeneity between compounds Re₂Te₂ and Re₂Te₅, presence of which was shown in [78, 80].

Thus, rhenium creates with tellurium a range of compounds appropriating to different stages of oxidation and most of these compounds can be obtained by direct interaction of rhenium and tellurium. For rhenium selenides are known following compounds: Re₂Se₇ (heptaselenide), ReSe₂ (diseleide), ReSe (monoselenide), Re₃Se₂ and Re₂Se₅. Re₃Se₅ (rhenium pentaselenide) was obtained by running H₂Se through solution of KReO₄ with addition of potash for linking of some amount of selenium discharging during the reaction. Rhenium diseleide ReSe₂ first was obtained by heating of Re₃Se in vacuum at 330 °C during 9 hours according to reaction:

\[
\text{Re}_2\text{Se}_7 \rightarrow 2 \text{ReSe}_2 + 3 \text{Se}.
\]

Obolonchik Ch.A. and Mikhlina T.M. proposed a method of obtaining rhenium diseleide by action of dry H₂Se to metallic rhenium or ammonium perrhenate [79]. The optimal temperature of synthesis in both cases is 700 °C.
The Electrochemical Deposition of Rhenium Chalcogenides from Different Electrolytes

Re + H₄Se = ReSe₂ + 2 H₂.
2 NH₄ReO₄ + 7 H₂Se = 2 ReSe₂ + 2 NH₃ + 8 H₂O + 3 Se.

Rhenium diselenide is stable in hydrogen flow at heating to 400 °C then, if the temperature continues to rise, selenium detaches and at the temperature 900 °C and more rhenium diselenide fully looses selenium and stays pure metallic rhenium.

The formation of rhenium selenide ReSe₂ is well confirming by roentgenographic examination of reaction products. In the work [85] was made roentgenographic examination of part of system Re-Se in an interval of concentrations 50-70% at. Se. To this aim were synthesized and examined samples having following composition: ReSe (50% at. Se), ReSe₂ (66.6% at. Se), Re₂Se₅ (71.43% at. Se) and ReSe₃ (75% at. Se). X-ray analysis of obtained samples showed that in examined range of system exists only one phase-ReSe₂. ReSe and Re₂Se₃ are dark grey roentgenomorphous powders. They do not dissolve in water and organic solvents.

ReSe₂ is a powder of black color, without smell with density (according to pycnometric test) being equaled 8.27 g/cm³. ReSe₂ is entirely stable on air, fully soluble while heated in hydrogen peroxide and in mixed of nitric and sulfuric acids. In concentrated HCl ReSe₂ does not dissolve as in cold so when heated. In nitric, sulfuric acids and in aqua regia it is partially soluble when heated. The solution in mixed HNO₃ and H₂O₂ begins at cold and entirely runs under heating. In 25% ammonia and ethyl alcohol rhenium diselenide does not dissolve. ReSe₂ is active catalyst for n-butane dehyration to divinyl (the temperature of the reaction ~650 °C).

At present there are known several methods of rhenium sulfides production. In system Re-S was defined existence of rhenium sulfides with composition: ReS, Re₂S₃, Re₃S₄, Re₅S₇ and Re₂S₇ [41, 85]. Only ReSe₂ of all rhenium sulfides can be produced by direct synthesis of components, other compounds are to be produced by indirect methods.

Most stable compound of rhenium with sulfur is ReS₂. In the works rhenium disulfide was obtained by direct interaction of elements in evacuated ampoules, and in the study of C. Odent [82] by dissociation of higher sulfides. It can be obtained by sulfidizing of metallic rhenium [82] rhenium oxides (ReO₂). ReS₂ is black powder, stable on air, has a density 7.506 g/cm³, it does not dissolve in H₂SO₄, in HCl, as well in alkali. The authors [49] supposed hexagonal one, MoS₂ type. Re₃S₄ (rhenium pentasulfide) is obtaining by long pumping of hydrogen sulfide through acidic (1-4 HCl) solution of perrenate [3] or in heated mixture of rhenium perrhenate and sodium thiosulfate solutions.

As seems from abovementioned, using these methods is possible to get rhenium chalcogenides in a form of massive samples or powder [83, 84]. As presently wide use in technique find rhenium chalcogenides in a form of thin films there are needed additional operations for conversion of abovementioned samples to obtain thin films. In connection with this an electrochemical method of production thin films of rhenium chalcogenides on conducting base takes on a distinctive importance.

The authors Sharipova N.S. and Songina O.A. [47] investigated electrochemical behavior of selenium (VI) with presence of rhenium (VII) at mercury dripping electrode. Was defined that rhenium (VII) in this condition shows one well defined wave in the range of potentials -0.35-0.8 *n.k.e. At joint presence of rhenium and selenium appears maximum at potential -0.7 V, no observed before separately for rhenium or for selenium, which carries catalytic character and which can be used as calibrate graph for quantitative definition of selenium.

We also have been studied semi-conducting coatings of chalcogenides rhenium from different electrolytes [66, 69-75, 81-83, 85-99].

For obtaining semi-conducting of Re-Se alloy we investigated joint electrodepositing of rhenium and selenium from alkaline [75] and sulfate [69, 70, 99] electrolytes. To obtain Re-Se alloy from sulfate
electrolyte [69, 99] was used the electrolyte with following composition (mole/L): 0.1-0.01 SeO₂ + 0.01-0.1 NH₄ReO₄ + 2.0 H₂SO₄, a current density 10 mA/cm², temperature 75 °C. For first time were defined main regularities of co-deposition of rhenium, selenium and rhenium by selenium from sulfate electrolyte. Was found, that under definite conditions of electrolyte the joint electrodeposition of rhenium and selenium takes place. At first time was carried out physics-chemical investigation of alloy forming in system Re-Se when joint electrodeposing rhenium and selenium from sulfate electrolyte. Basing on the experimental data was proposed the interpretation of cathodic process carrying out at various meanings of cathodic potential. Basing on experimental data was developed optimal composition of electrolyte and electrolysis regime for obtaining quality semi-conducting coatings of rhenium chalcogenides from sulfate electrolyte [99]. For obtaining Re-Se alloy from alkaline electrolyte we used the electrolyte following composition (mole/L): 0.01-0.1 M NH₄ReO₄ + 0.01-0.1 M SeO₂ + 1-3 NaOH alkaline electrolytes.

At first time using potentiostatic, temperature-kinetics and voltammetric methods were investigated kinetics and mechanism of separate and joint electrodeposition of rhenium with chalcogenes from sulfate electrolyte [75]. It was defined that the mechanism of joint electrodeposition of rhenium with selenium from alkaline electrolyte depends of concentration of bivalent selenium obtained on cathode, which optimizes reduction of rhenium with forming of chemical compounds ReSe₂. At a cathode current density of 4 mA/cm², using an electrolyte of composition 0.05 M NH₄ReO₄ +0.05 M SeO₂ + 1 M NaOH, we obtained lustrous ReSe₂ (54 wt% Re) coatings. The formation of ReSe₂ was confirmed by XRD. At first time were investigated some physics-chemical properties of thin coatings of Re-Se alloys.Re-Te alloy we proposed and chloride-sulfate [91, 97] electrolytes. For obtaining semi-conducting alloy Re-Te in a form of thin films was found optimal regime and electrolyte. For obtaining thin films of rhenium chalcogenides in the work was proposed the electrolyte and optimal regime for producing alloys. To obtain thin films ReTe₂ (rhenium ditelluride) is necessary to carry out electrolyses at current density 2 mA/cm², temperature 75 °C from electrolyte .

It was proposed an electrolyte and optimal regime to get rhenium-tellurium thin films in chloride-borate electrolyte [93, 94, 96] for obtaining alloys Re-Te. Using potentiostatic, temperature-kinetic, voltammetric methods were investigated kinetics and mechanism of separate and co-electrodeposition of rhenium and tellurium from chloride-borate electrolyte. Was defined that a discharge of tellurium complex on cathode runs through occurring of intervening particles, arriving as a result of preceding chemical reaction of tellurium complex dissociation. At co-deposition of rhenium and tellurium from chloride-borate electrolyte a main role plays a chemical activity of tellurium connected with its disposal to deep deoxidation and formation of Te²⁻ at the surface of a cathode. It changes a nature of tellurium electrode and leads to co-electrodeposition of rhenium and tellurium with formation of chemical compound ReTe. It was found that finely crystalline, glittering coatings with a composition of ReTe₂ (42 wt% Re) and a thickness of up to 5 μm formed from the electrolyte containing (M) 0.05 NH₄ReO₄ + 0.003 TeO₂ + 3 HCl + 0.05 H₃BO₃ (electrolysis time 30 min, current density 1.2 A/dm², 0.25-0.20 V, s.c.e.). According to X-ray phase analysis data, ReTe₂ crystallized as an orthorhombic compound with unit cell parameters \( a = 1.301 \) nm, \( b = 1.307 \) nm, and \( c = 1.428 \) nm [94].

Alloys of rhenium and sulfur are using as a photosensitive material in semi-conducting technique in a form of coatings. In works [72, 93-94] was widely investigated co-electrodeposition of rhenium and sulfur from sulfate and thiosulfate electrolyte [87]. Using the method of voltammetry was investigated a
process of electrodeposition of rhenium sulfide films at platinum and titanium cathodes. Was proposed the mechanism of this process including electro-deoxidation of Re(VII) to Re(0) and chemical interaction of Re with S. Was defined that to quality and composition of films substantially influences a concentration of main components in electrolyte, a temperature, current density and acidity of electrolyte. Using X-ray testing was proved that in co-electrodeposition of Re and S at cathode is forming chemical compound of rhenium disulfide ReS₂. It was defined that obtained coatings have p-tip conductivity. The electrodeposition of thin films Re-S from aqueous solutions containing ammonium perrhenate, thiocarbamide and sulfuric acid was made in the work [72]. The electrolytic alloys Re-S were obtained from the electrolyte of the following composition: 0.1 × 10⁻³-2.0 ×10⁻³-MN₄ReO₄; 1 × 10⁻³-3 × 10⁻³ M(NH₂)₂CS; 0.5 × 10⁻³-1.23 × 10⁻³ MH₂SO₄; pH = 1-1.5, current density being 25-45 mA/sm².

At first time was physical-chemical investigation of alloy formation in Re-S system and was defined that co-electrodeposition of rhenium and sulfur depends of adsorption of colloidal sulfur on cathode, and as rhenium so sulfur deposit by depolarization which affirms the formation of chemical compound ReS₂.

The rhenium alloys have found wide application in radio technique, electronics, semi-conducting industry and other fields of modern technique. In this connection undoubted practical and theoretical interest has the electrochemical deposition of rhenium.

Also in the review indicates that the rhenium alloys are widely used in electronics, electrical engineering, electronics and semiconductor industry and other areas of modern technology. Thus, from abovementioned review is clear that acidic and alkaline solutions are good electrolytes for the production of coatings of rhenium alloys.

Therefore, a detailed study of the process of co-electrodeposition of rhenium with chalcogenides of alkaline and acidic electrolytes has practical and theoretical interest.

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