

The Investigation of Microstructure and the X-Ray Phase Analysis of Re-X Alloys (X = S, Se, Te)

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Abstract

Influence of terms electrolysis and concentration of electrolysis components on the microstructure obtaining films of the chalcogenides rhenium has been studied. Appearance and structure electrolytical depositions of chalcogenides rhenium, obtaining by electrochemical method, depend from electrolysis conditions. In the process of studying of electrolysis conditions has determined that for obtaining qualitative depositions of rhenium chalcogenides most suitable temperature is 75°C - 80°C. Microscopic studying of surface of cathodic deposition of Re-Se showed that on the cathode had been obtained dense fine-crystalline black coverings. More qualitative depositions have been obtained for low current density. Increasing if current density adducts to gradual deterioration of structure cathode depositions. It has been determined that specific influence on the process of deposition Re-S alloys has changing of electrolyte pH and current density. At low pH values, the colloidal sulfur formed in electrolyte has adsorbed on the cathode and bearing to the deposits quality. Microscopic studying of surface of cathode depositions Re-Te₂ showed that on the cathode at current density 2 mA/sm² had been obtained dense grey fine crystalline deposits of ReTe₂.

Keywords

Electrochemistry, Rhenium Chalcogenides, Microstructure, Electrodeposition, Alloys Films

1. Introduction

Metallic rhenium and it's alloys have unique physico-chemical properties, due to winch find wide application in

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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 [3]. Thus the application of catalysts of mentioned type provided 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. We also have been studied semi-conducting coatings of chalcogenides rhenium from different electrolytes [7]-[13].

For obtaining semi-conducting of Re-Se alloy, we investigated joint electrodeposition of rhenium and selenium from alkaline [7] and sulfate [10] [11] electrolytes technique [7] [11]. Re-Te alloy, we proposed and chloride-sulfate [11] 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. An electrolyte and optimal regime to get rhenium-tellurium thin films in chloride-borate electrolyte [8] for obtaining alloys Re-Te was proposed. Using potentiostatic, temperature-kinetic, voltammetric methods were investigated kinetics and mechanism of separate and co-electrodeposition of rhenium and tellurium from chloride-borate electrolyte. Alloys of rhenium and sulfur are using as a photosensitive material in semi-conducting technique in a form of coatings. Work was widely investigated co-electrodeposition of rhenium and sulfured from sulfate and thiosulfate electrolyte [9]. Using the method of voltammetry, a process of electrodeposition of rhenium sulfide films at platinum and titanium cathodes was investigated. 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.

The physical-mechanical properties of electrolytic deposits are essential characteristics of coatings quality and determine their applicability to a particular area of technology. Properties of the electrolytic deposits are determined by the presence of inclusions in these deposits various foreign particles, as well as by the degree of irreversibility of the electrode process in the reduction of the ions of metals. This circumstance is due to the fact that the reducible ions, passing through an electric double layer having a large electric field intensity, become higher speed, which he immediately loses upon entering the crystal lattice, it leads to the formation of non-equilibrium lattice with changes of its parameters.

It's necessary to note some interesting capabilities opening when the joint discharge of metal ions takes place meaning a possibility of obtaining coatings with properties that cannot be created in other ways. So, by the electrolytic deposition is possible to obtain alloys that by crystallization from a molten state cannot be obtained.

Alloys obtained by electrolysis, are nonequilibrium and differ sharply in structure from the alloys produced by thermic method. Therefore, the equilibrium state diagram cannot mechanically transferred to an alloy obtained by electrolysis as depending on the method of producing alloys differ both in structure and in properties. Deposits obtained electrolytically contain both metal inclusions and a large number of non-metallic inclusions, namely hydroxides, oxides, hydrogen, halogens, surfactants and others. With it are linked their special physical-mechanical properties.

In this work, we represent [7]-[12] carried out the main regularities for mutual electrodeposition of thin semi-conducting films of the rhenium chalcogenides from different electrolytes, also some data about microstructure rhenium chalcogenides obtaining by electrochemical methods were represented. Some of these data obtaining in the results carried out researches have got scientific interest. We think it is necessary to involve in the chamber, these data confirming implemented research.

2. Methods of Experiment

X-ray studies of cathode deposits were carried out by automatic recording of roentgenograms on the tape at rotation speed of the sample 2°C per minute on the X-ray machine DRON-4.

The structure of the surface and the cross-sections of cathode deposits of Re-X (X = S, Se, Te) was studied using a scanning electron microscope Testa Bs-301. Before polishing of the transverse sections of deposits they were coated by epoxy resin and after solidification of powders they were polished by chrome paste and etched

with a solution of iodine in ethanol. A thickness of films was measured by interference method using MII-4 with standard error of 0.4 microns. Phase analysis of the deposits with low content of rhenium chalcogenides was also performed on the P-5827M potentiostat getting the polarization curves of the anodic dissolution of the alloy. Adhesion of cathode deposits with the cathode surface was tested by scratching and bending of the electrode at an angle of 90 degrees, the porosity of the coating was determined by applying filter paper.

Proceeding from the data it should be noted that thin films of rhenium chalcogenides possess rather low values of temperature coefficient and electroresistance what allows to apply such films in electronic technics.

3. Results and Their Discussion

The possibility of the obtaining of electrolytic coatings with a various desired properties contributed to the expansion of their application in industry.

Was investigated the microstructure of the cathode films of rhenium chalcogenides Re-X (X = S, Se, Te), obtained by the electrochemical method from various electrolytes. Was studied the influence of electrolysis conditions and the concentration of electrolyte components on the microstructure of produced rhenium chalcogenides films. The appearance and structure of the electrolytic deposits of rhenium chalcogenides obtained by the electrochemical method, depends on the conditions of electrolysis.

3.1. Re-Se

In the process of studying the electrolysis conditions was found that for obtaining of high-quality alloys Re-Se, most suitable temperature is 75°C - 80°C. Microscopic study of the surface of the cathode deposits Re-Se showed that the on the cathode are obtaining dense microcrystalline black coloured coatings. Particularly strong influence on the quality of the deposits has a current density. Higher-quality deposits are obtaining at low current densities. Increasing the current density leads to a gradual deterioration of the structure of the cathode deposits. As can be seen from **Figure 1**, at low current densities (1 - 5 mA/cm²) on the cathode are obtaining glossy fine-grained deposits having thickness of 5 microns. At a current density higher than 10 mA/cm² at the cathode are formed rather friable black deposits easily sleeping off from the metallic substrate.

A similar effect of current density on the appearance and structure of electrolytic deposits ReSe₂ can be explained as follows: at a current density below the limit, delivery of ions to the surface of the electrode is not limited by diffusion, and related crystallization rate is satisfactory. However, with achieving a zone of limiting current density the delivery of ions to the cathode surface is hampering affecting the crystallization rate. Due to the reduction of the number of ions discharging at the cathode, the electrode surface is partially passivated, crystallization occurs at the active sectors.

As the result are forming spongy and rather friable deposits in the form of randomly oriented microcrystalline aggregates, weakly bound between themselves and with the surface of the cathode.

The same effect on deposits quality has rise of the temperature of the electrolyte, as this also increases the area of current densities at which high-quality deposits are forming.

Photomicrograph of cross section of a platinum cathode with the deposit having the composition 54% Re + 46% Se showed that deposit consists of single phase.

For production of thin coatings of alloy Re-Se from acidic electrolyte was used an electrolyte of the following composition (mol/l): 0.05NH₄ReO₄ + 0.05SeO₂ + 2.0H₂SO₄ at a current density of 4 mA/cm² [10].

Both in the alkaline and acidic electrolytes at the cathode are obtaining fine-grained deposits of alloy of Re-Se with different composition and with changing of the conditions of electrolysis changes a quality of deposits.

Thus, with increasing of the current density from 1 to 4 mA/cm² on the cathode are forming deposits of alloy Re-Se 10 microns thick, black-gray colored.

With increasing of current density above 5 mA/cm² the quality of cathode deposits deteriorates, on the cathode form friable, black deposits of alloy Re-Se. There were analyzed the content and morphology of thin layers ReSe₂, electrodeposited on the platinum electrode. From the X-ray phaseous analysis it follows the film consist from 54% of Re and 46% of Se (according to the mass). The diagram of X-ray phaseous analysis of the film ReSe₂ is presented in **Table 1**.

We have established that the compound ReSe₂ is crystallized in triclinic syngony with the parameters of the lattice: a = 6.7275 Å; b = 6.6065 Å; c = 6.7196 Å (**Table 1**).

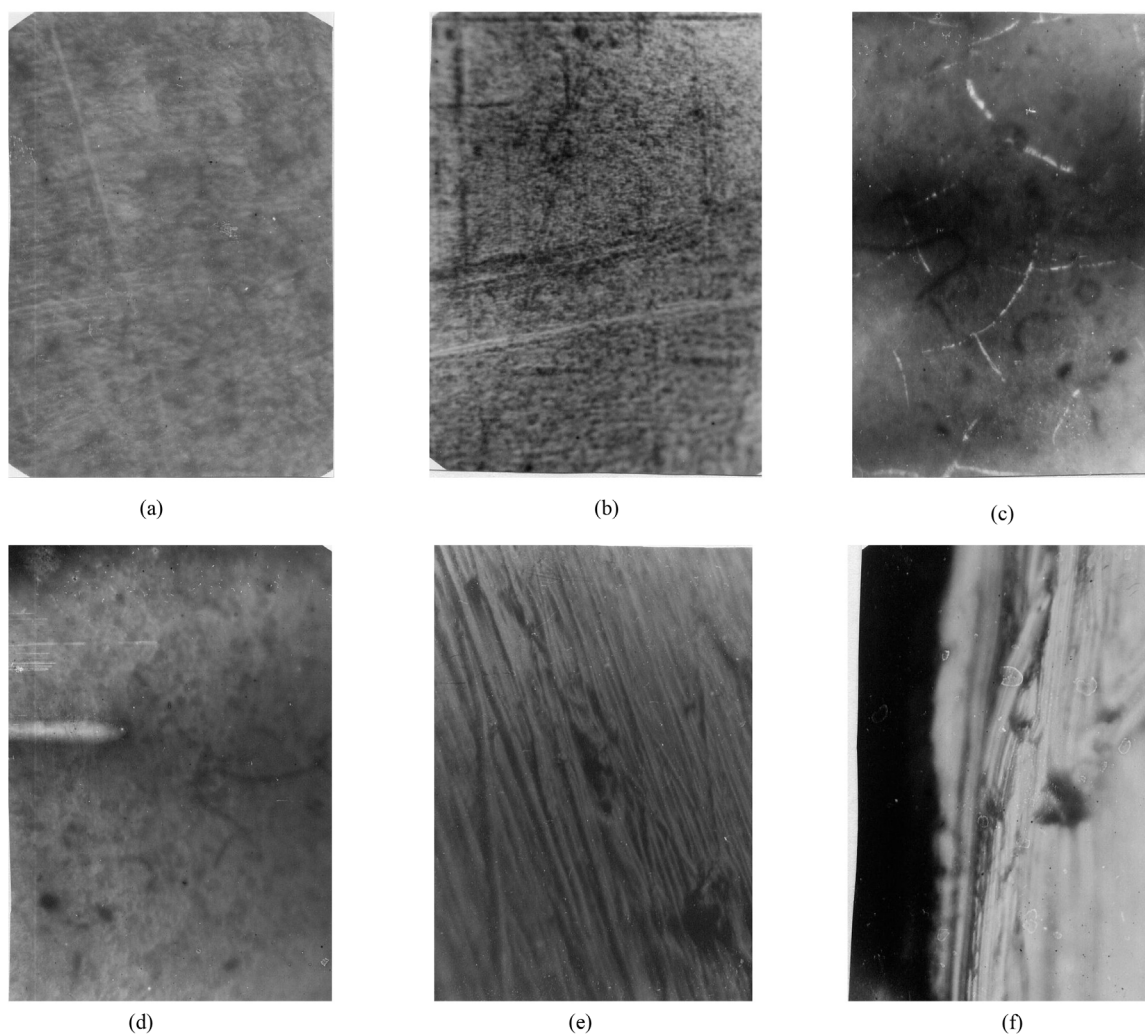


Figure 1. The microstructure of cathode deposits Re-Se (500×) obtained for different current densities (mA/cm²): (a) 2; (b) 5; (c) 8; (d) 10; (e) 15; (f) Transverse section micrograph of the alloy composition of the ReSe₂ (500×).

Table 1. Value of interplane distances and intensity for compound ReSe₂ obtained from sulphate electrolyte. Composition of electrolyte (mol/l): 0.035NH₄ReO₄ + 0.25SeO₂ + 2.0H₂SO₄ (Jc = 15 mA/sm², and t = 75 °C).

d, nm	J/J ₀	hkl	d, nm	J/J ₀	hkl
6.38	90	100	2.214	20	112
5.781	40	001	2.205	40	121
4.720	40	101	2.183	40	023
3.240	20	0.11	2.163	40	131
2.867	60	120	2.143	20	012
2.696	20	211	2.100	40	021
2.510	90	220	2.075	20	031
2.480	40	-	2.043	40	212
2.469	100	122	2.015	20	320
2.370	40	202	1.947	60	103
2.272	40	127	1.880	40	213

3.2. Re-S

This work is devoted to research of microstructure of a cathode precipitation of Re-S obtained by electrodeposition from sulfate thiureous solutions, containing (mol/l): 2.2×10^{-3} NH_4ReO_4 ; $(\text{NH}_2)\text{CS}_2$ 1.0×10^{-3} , H_2SO_4 1.23×10^{-3} [9].

Study of influence of electrolysis conditions on a microstructure of obtained films confirmed the assumption of the mechanism of joint sedimentation of rhenium with sulfur.

It is established that change of electrolyte pH and current density has special influence on process of sedimentation. At low pH values the colloidal sulfur formed in electrolyte has adsorbed on the cathode and bearing to the precipitation quality.

During researches it was established that depending on conditions, at the low density of current the multi-phase precipitation were of dark color with brown, red and blue fragments, with yellow crystal dissemination.

Apparently, at the low current density the insignificant quantities of Re_2S_7 (brown color), ReO_2 (red color), Re_2S_5 and S elementary (yellow color) are the products of electroreducing. Formation of rhenium oxides and Re_2S_7 can be explained to that at the low density of current delivery of perrenate ions to a surface of the cathode and their discharge is complicated.

Availability of crystal sulfur, obviously is connected with that wish at the low density of current the potential of sulfur reducing to sulfide ion isn't reached.

At increase of current density to its limit value, character of a surface of films sharply changes. At the current density of 30 mA/cm^2 (at optimum conditions) the film looks like a single-phase uniform micro crystallographic deposit of rhenium disulfide. In these conditions the speed of the discharge of ReO_4 isn't limited by diffusion and the crystallization speed related with it is satisfactorily. At further increase in density of current the precipitates remains single-phase, but in this case they characterized by friability.

The microphotography of a cross section of the platinum cathode with a deposit of the following composition, wt %: Re = 74.4; S = 25.6 showed that the deposit consist of one phase (Figure 2) and its structure corresponds to ReS_2 compound.

With the aim of clearing out the crystalloid structure of the obtained thin coverings ReS_2 , there was carried out their X-ray graphical investigation.

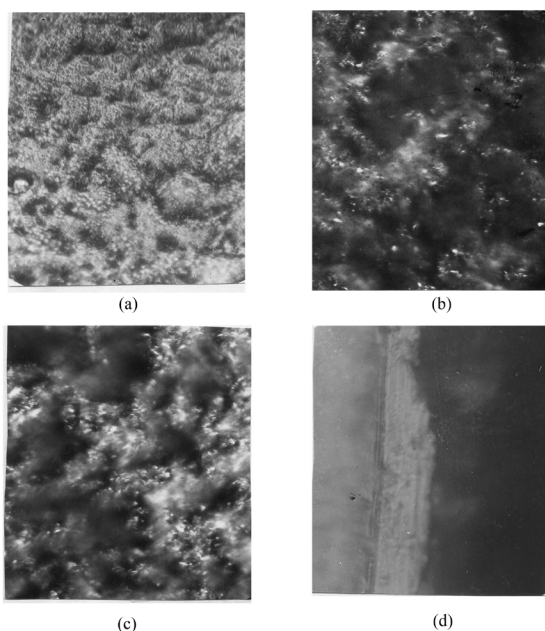


Figure 2. Microstructure of a cathode precipitation of an Re-S alloy, obtained at the various density of current (mA/sm^2): (a) 30; (b) 35; (c) 40; (d) Microphotography of cross section of the platinum cathode with an alloy of ReS_2 structure (500 \times).

According to RPA it was established, the ReS_2 complexes are crystallized in a triclinic syngony with the parameters of elementary cell: $a = 6.455 \text{ \AA}$, $b = 6.363 \text{ \AA}$, $c = 6.4$ (**Table 2**).

3.3. Re-Te

Was studied the micro-structure of Re-Te alloy, obtained from chloride-sulfates electrolyte with complexation.

Was studied effect of current density from 1 to 10 mA/cm^2 to appearance and micro-structure of cathode deposits.

Microscopic study of the surface of the cathode deposits Re-Te showed that on the cathode at a current density of 2 mA/cm^2 are obtaining dense fine-grained coatings ReTe_2 .

As it can be seen from **Figures 3(a)-(c)**, with an increase in current density the structure of the cathode deposits gradually deteriorating. In this case, at a current density of 8 mA/cm^2 at the cathode are obtaining rather friable coatings easily falling off from metallic surface.

In order to obtain the thin, smooth coatings of ReTe_2 alloy, the electrolysis should be carried out at a current density of 2 mA/cm^2 at temperature of 75°C from the electrolyte with the composition (mol/l): $0.03\text{NH}_4\text{ReO}_4 + 0.03\text{TeO}_2 + 1.5\text{HCl} + 1.5\text{H}_2\text{SO}_4 + 0.01(\text{NH}_4)_2\text{SO}_4$ [13].

In this case at the cathode are obtaining compounds of single-phase coating ReTe_2 , wherein the rhenium content is 42%, cross-sectional micrographs of a platinum electrode with the composition showed 42% and 58% rhenium tellurium that the precipitates consist of one phase (**Figure 3(d)**).

It was found that finely crystalline, glittering coatings with a composition of ReTe_2 (42 wt% Re) and a thickness of up to 5 \mu m formed from the electrolyte containing (M) $0.03\text{NH}_4\text{ReO}_4 + 0.03\text{TeO}_2 + 1.5\text{HCl} + 1.5\text{H}_2\text{SO}_4 + 0.01(\text{NH}_4)_2\text{SO}_4$ (electrolysis time 30 min, current density 1.2 A/dm^2 , $0.25 - 0.20 \text{ V}$, s.c.e.). According to X-ray phase analysis data, ReTe_2 crystallized as an orthorhombic compound with unit cell parameters $a = 1.301 \text{ nm}$, $b = 1.307 \text{ nm}$, and $c = 1.428 \text{ nm}$. **Figure 4** shows the X-ray spectra of the ReTe_2 alloy on a platinum electrode. **Table 3** lists the interplanar distances and intensities for the ReTe_2 compound obtained from the chloride-sulfate electrolyte.

In the conclusion that the co-deposition of rhenium with tellurium occurs with minor depolarization. The magnitude of depolarization depends on the energy liberated during the alloy formation.

4. Conclusions

- 1) The process of studying of electrolysis conditions has determined that for obtaining qualitative depositions of rhenium chalcogenides, most suitable temperature is $75^\circ\text{C} - 80^\circ\text{C}$.

Table 2. Value of interplane distances and intensity for compound ReS_2 obtained from sulphate electrolyte. Composition of electrolyte (mol/l): $1 \times 10^{-3} \text{ NH}_4\text{ReO}_4 + 1.5 \times 10^{-3} (\text{NH}_4)_2\text{CS} + 1.23 \times 10^{-3} \text{ H}_2\text{SO}_4$; $i_k = 30 \text{ mA/cm}^2$.

d, nm	J/J ₀	hkl	d, nm	J/J ₀	hkl
6.381	95	001	1.892	30	202
5.262	20	110	1.763	20	121
3.423	20	101	1.620	80	221
2.982	10	102	1.585	10	222
2.861	30	112	1.479	20	130
2.743	95	200	1.466	10	302
2.301	100	201	1.448	10	204
2.254	50	202	1.419	10	224
2.132	70	121	1.411	10	023
2.096	60	321	1.386	30	041
2.067	20	231	1.366	20	402

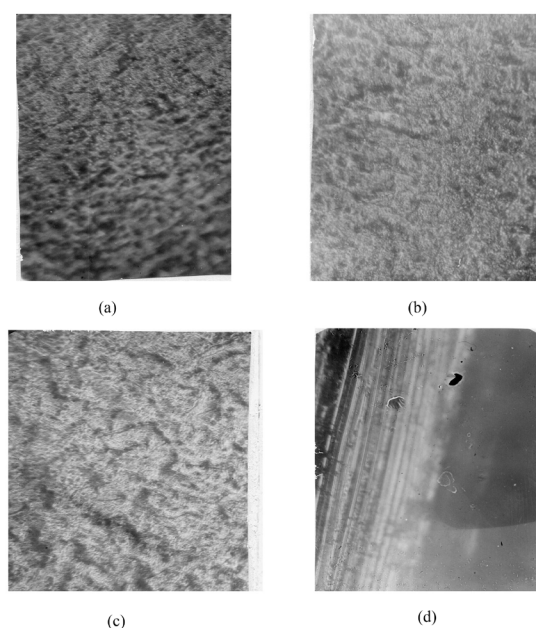


Figure 3. The microstructure of cathode deposits Re-Te (500 \times) obtained for different current densities (mA/cm²): (a) 2; (b) 5; (c) 8; (d) Transverse section micrograph of the alloy composition of the Re-Te (500 \times).

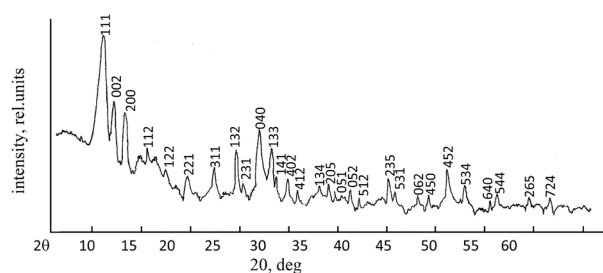


Figure 4. X-ray diffraction pattern of ReTe₂ alloy electrodeposited on a Pt electrode at 75°C (current density 2 mA/cm²). The composition of the film was 42% Re and 58% Te (film thickness 5 μ m).

Table 3. Interplanar distances and intensities for ReTe₂ obtained from a chloride-sulfate electrolyte.

	J/J_0	hkl	d , nm	J/J_0	hkl
0.7748	100	111	0.2608	20	205
0.7138	50	002	0.2564	10	051
0.6511	60	200	0.2455	25	052
0.5644	25	112	0.2404	20	512
0.4524	20	122	0.2238	35	325
0.4383	25	221	0.2201	25	531
0.3938	30	311	0.2082	10	062
0.3573	40	132	0.2036	15	450
0.3506	15	231	0.1956	40	452
0.3271	50	040	0.1888	20	534
0.3121	40	133	0.1801	10	640
0.3089	25	141	0.1769	15	544
0.2959	30	402	0.1675	10	265
0.2885	20	412	0.1595	10	724
0.2694	15	134			

- 2) Microscopic studying of surface of cathodic deposition of Re-Se showed that on the cathode had been obtained dense fine-crystalline black coverings. More qualitative depositions have been obtained for low current density. Increasing if current density adducts to gradual deterioration of structure cathode depositions. It has been determinated that specific influence on the process of deposition of Re-S alloys has changing of electrolyte pH and current density.
- 3) Microscopic studying of surface of cathode depositions Re-Te₂ showed that on the cathode at current density 2 mA/sm² had been obtained dense grey fine crystalline deposits of ReTe₂.

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