



Electrodeposition rhenium-tellurium alloys from chloride acid electrolytes.

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Abstract

There has been investigated the joint electrodeposition of rhenium with tellur from chlorides electrolyte, by measuring the cycling volt-ampere curves there has been determined the field of potentials, at the presence of which the joint electrodeposition of rhenium with sulphur takes place. It has been shown, that the joint deposition of rhenium with tellur goes with a certain depolarization, besides, the depolarization is caused by the energy emanating along formation of ReTe_2 compounds. There was studied the influence of current density, temperature and acidity on the composition and quality of cathode sediments. It was established, that with the rise of current density and the temperature of electrolyte the concentration of rhenium in the alloy increases.

Keywords: rhenium chalcogenides, semi-conducting materials, electronic technique.

Date of Submission: 2018-06-01

Date of Acceptance: 2018-06-20

Date of Publication: 2018-07-04

DOI 10.24297/jac.v15i2.7454

ISSN: 2321-807X

Volume: 15 Issue: 02

Journal: Journal of Advances in Chemistry

Website: <https://cirworld.com>



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Introduction

The electro-chemical obtaining of semi-conducting compounds in the form of thin films of rhenium chalcogenides on various base layers took greater and greater importance in a connection with intensive development of an electronic technique. [1-4].

Rhenium chalcogenides alloys are semi-conducting materials and are being used as photo-sensitive element working in a visible range of the spectrum.

Basing on an investigation of a process of a joint electric sedimentation of rhenium and chalcogenes was developed a process of an obtaining semi-conducting alloys Re-X from acidic and alkaline electrolytes in a wide range of component ratio. Were determined optimal compositions and regime of electrolyte providing obtaining of high-quality semi-conducting alloys based on rhenium. Were investigated some physics-chemical and electro-physical properties of thin coats of rhenium chalcogenides' alloys.

Semi-conducting properties of diode structure based on rhenium chalcogenides- alloys showed that in alloys is being observed a controlled bipolar reversing effect. Gadgets, having these properties, may find wide use in electronics, radio-electronics and IT spheres. Rhenium chalcogenides' thin coatings are being used in high-speed operational memory.

Were determined photo-electrical properties rhenium chalcogenides' thin coatings and established possibilities of a further use of these films as a photo-electronic material for conversion of solar energy into a chemical one. The investigation results are recommended for diodes production in the radio-electronic industry. [5-6].

In future rhenium coating may be also used as a catalyst in oil refinery industry. A using of rhenium would allow to prolong a working time of the catalyst to five times comparing with now using ones. In future using various electro-chemical methods there would be possible investigate in more details a reaction mechanism and kinetics, find out regulations and particularities of rhenium and chalcogenides' electrical sedimentation, their properties with a purpose to develop recommendations for theoretical and practical use of obtained results.

Materials and methods

To obtain Re -Te alloy we used solutions of ammonium perrhenate, tellurium oxide, in chloride acid as an electrolyte. For obtaining of an alloy we used platinum electrode with 4cm^2 area as a cathode, but for polarization measurements we used platinum electrode with 0.15cm^2 area. As a comparative electrode we used silver-chlorine electrode, as an auxiliary electrode we used platinum plate. Potentiostatic curves were plotted in P-5827M potentiostat with KSP-4 potentiometer, cyclic voltampermetric curves were plotted with IVIUMSTAT potentiostat with 50ml glass electrolizer covered with glass coat. Temperature was controlled at $\pm 0.1^\circ\text{C}$ accuracy by U-10 thermostat. pH of solution was measured with Az86551 device.



The content of Re-Te alloy components has been analyzed as the following: 10 ml of concentrated HNO_3 were dissolved while heating and after repeated evaporation in the water boiler-both there was added 5 n of H_3PO_4 to the solution. The obtained solution has been diluted in the measured retort till 50 ml and then by extraction with isoamyl spirit rhenium was separated from selenium. The rhenium has been determined by photometry of rodanide complex at the device SPECORD 50 Plus [7], and tellurium has been determined by thiocarbomide complex [8].

X-ray graphical investigations of thin films Re-Te have been carried out at diffractometer URS-55 in CuK_α -irradiation in RKD camera 57,3.

Results and discussion

To study co-electrolytic process of rhenium tellurium the deposition process of these metals from separate electrolyte must be studied. For this purpose we studied electrolytic deposition of rhenium, tellurium and copper from chloride solutions.

We studied electrolytic deposition of rhenium from chloride solutions and it was determined that in chloride electrolyte rhenium is in the form of perrhenate ion (ReO_4^-) and reduction of rhenium goes in stages [7-10]. We studied the effect of density, temperature of rhenium, acidity of solution in electrolyte, conversion rate of potential on polarization curves. (Fig. 1). Reduction of rhenium goes in several separate process and loadlessness of ReO_4^- ion goes in stages and results in formation of intermediate products.

Thus, reduction of rhenium from strong acidic electrolytes results in formation of intermediate oxide layers and this is confirmed by existence of oxide layers and red and blue color in deposit. By studying effects of density of rhenium, chloride acid, temperature, conversion rate of potential we selected optimum condition and necessary electrolyte to obtain high-quality rhenium deposits from chloride electrolyte. Electrolytic deposition process of tellurium from chloride solutions was studied. The most useful electrolyte is chloride electrolyte for deposition of tellurium from acidic medium (Fig.2.)

We studied the influence of electrolytic deposition of tellurium from chloride acid on polarization curves, density of tellurium in electrolyte, temperature, conversion rate of potential.

Reduction of tellurium ion goes according to the following way: the first stage of electrode process is determined by formation of elementary tellurium. In the second stage divalent tellurium is formed. In the third stage of electrode process we observed the formation of hydrogen. In reduction of tellurium ion we studied the effect of temperature on electrode process in stable value on cathode potential to determine the polarization nature of cathode.

Then we studied co-electrolytic deposition of Re with Te in chloride solutions and polarization curved were plotted. According to long-term experiments we studied electrochemical obtaining of Re-Te alloy and during deposition process obtaining of ReTe_3 , Re_2Te_5 compound was confirmed. To confirm the obtained results and to clarify kinetics and mechanism of co-deposition process of Re with Te anodic curves were plotted. (Fig.3.)



The properties of the deposited alloy markedly change with the electrolyte temperature. The deposits obtained at room temperature are nonuniform and have poor adhesion to the cathode surface; the dark gray deposits of the Re—Te alloy formed at 75—80°C, however, are monophasic and have good adhesion with the surface. Further experiments on codeposition of rhenium with tellurium, therefore, were performed at 75—80°C.

It was found that finely crystalline, glittering coatings with a composition of ReTe_2 (42 wt % Re) and a thickness of up to 5 μm formed from the electrolyte containing (M) $7 \cdot 10^{-3} \text{KReO}_4 + 1,25 \cdot 10^{-2} \text{TeO}_2 + 2\text{HCl}$. 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 $c = 1.428 \text{ nm}$. Results of experiments morphology films are shown in figure 4. It was determined that sizes of substances obtained in samples of Re-Te vary in 80-150 nm on platinum electrode.

Conclusion

We can thus draw 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.

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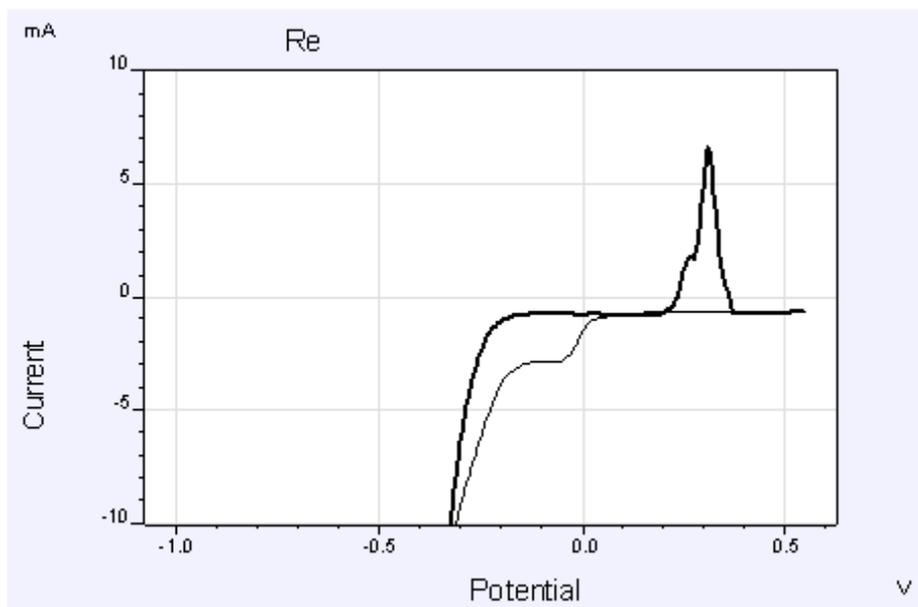


Fig.1. Volt-ampere cyclic polarizing curves of rhenium from chlorid solutions on the platinum electrode in the electrolyte contest, mol/l: $3,5 \cdot 10^{-3} \text{KReO}_4 + 2\text{HCl}$ at $t=75^\circ$; $V=0,005\text{V/S}$; $\text{pH}=0,4$

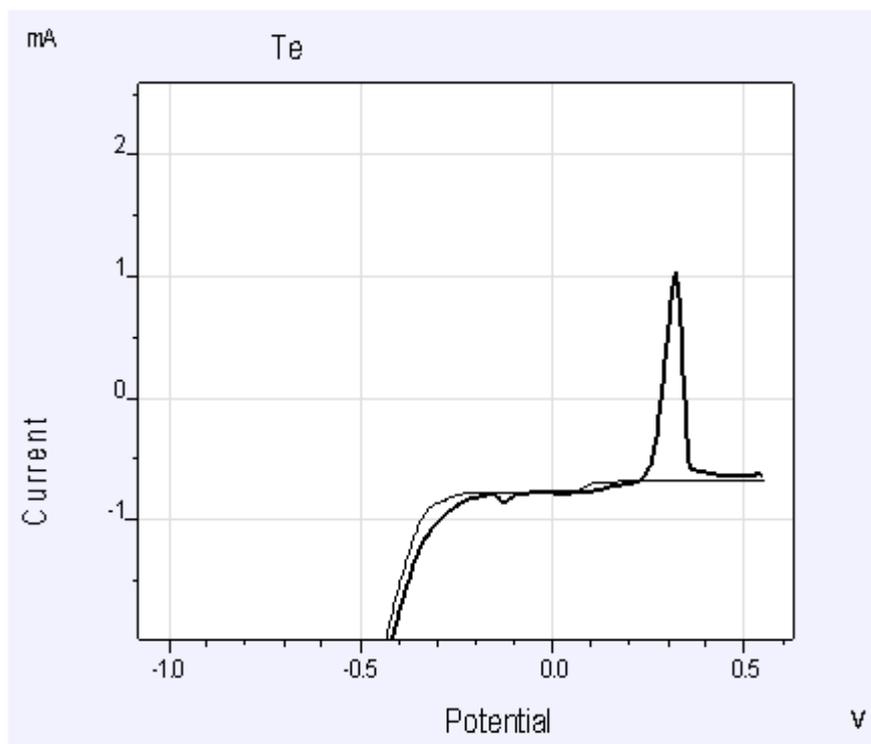


Fig.2. Volt-ampere cyclic polarizing curves of tellurium from chlorid solutions on the platinum electrode in the electrolyte contest, mol/l: $0,6 \cdot 10^{-2} \text{TeO}_2 + 2\text{HCl}$ at $t=75^\circ$; $V=0,005\text{V/S}$; $\text{pH}=0,4$

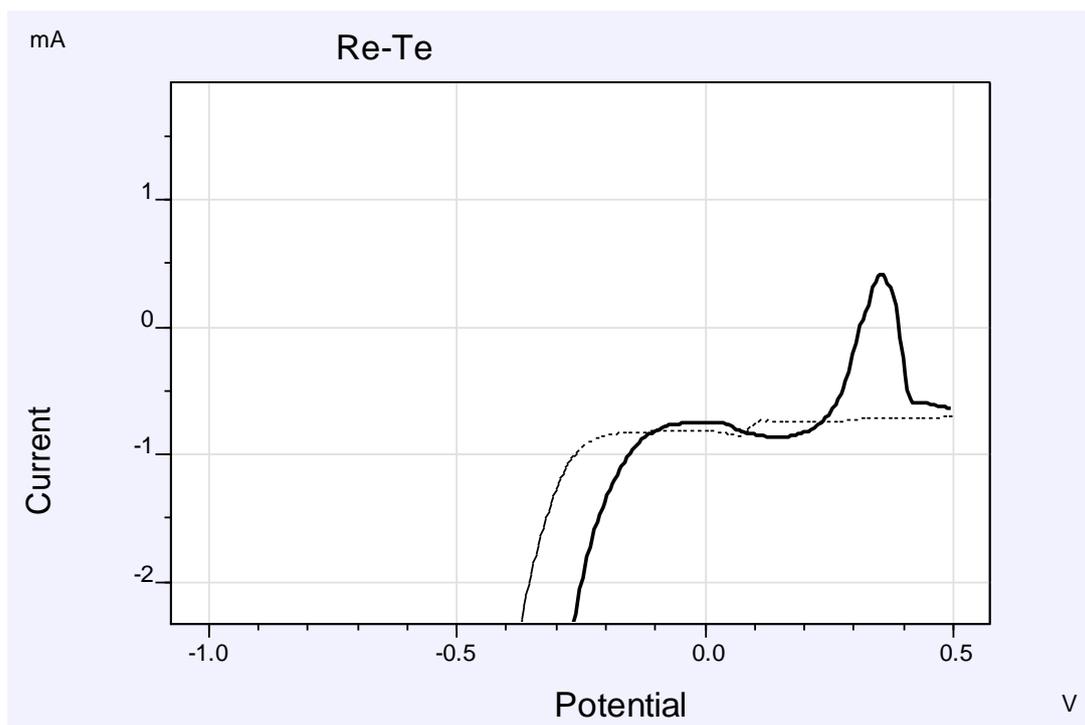


Fig.3. Volt-ampere cyclic polarizing curves of Re-Te alloy from chlorid solutions on the platinum electrode in the electrolyte contest, mol/l: $7 \cdot 10^{-3} \text{KReO}_4 + 1,25 \cdot 10^{-2} \text{TeO}_2 + 2\text{HCl}$ at $t=75^\circ$; $V=0,005\text{V/S}$; $\text{pH}=0,4$

Chemical Element	Weight ratio %	Atomic ratio, %
Te-L	69,05	76,50
Re-M	30,95	23,50
Amount	100	

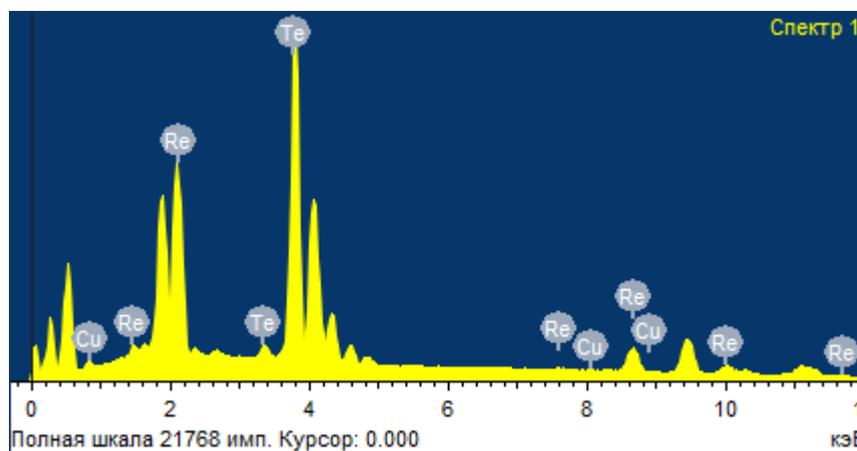
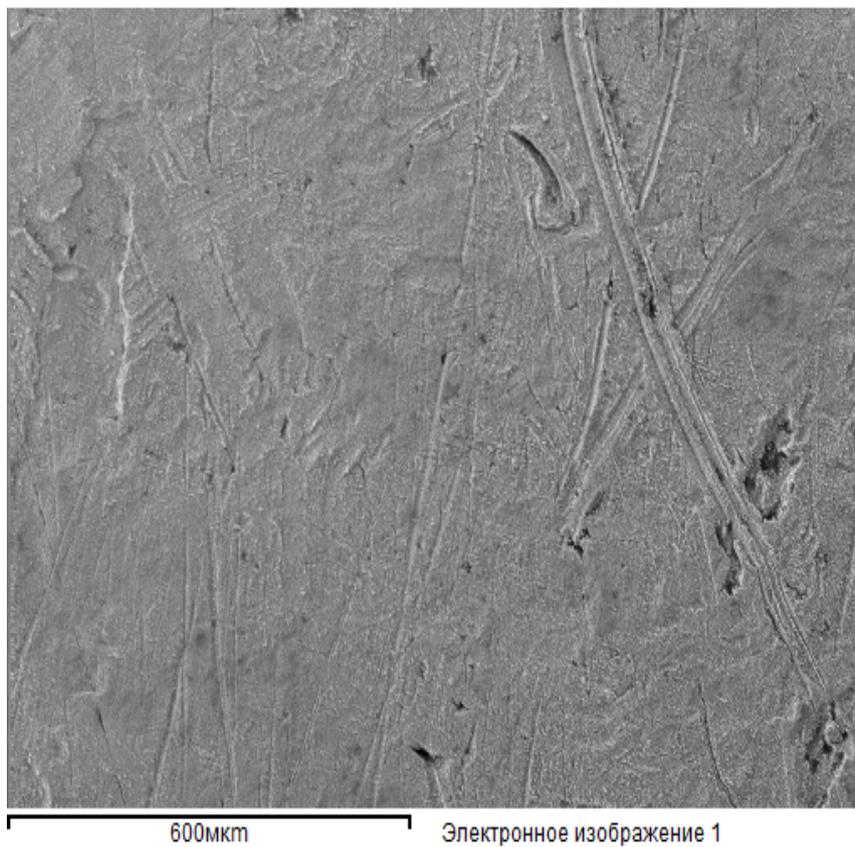


Fig 4. Analysis SEM for obtained thin films in the system Re-Te during 1800 seconds on the platinum electrode at +0,5V potential and $t=343^\circ$