

*Short Communication*

## **Formation of Thin Rhenium Films on Nickel Plate by its Chloride Electrolysis**

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Rhenium electrodeposition from aqueous solutions of HCl was studied. The electrode deposits were obtained by the galvanostatic electrolysis. It is established that a rhenium film may be formed by the electrolysis of the rhenium containing aqueous solutions of hydrochloric acid. According to the scanning electron microscopy the film consists of rhenium clusters. The film structure does not have any microdefects and it may be used for the further rhenium electrodeposition.

**Keywords:** microcrystalline rhenium, composite, electrodeposition, aqueous solutions, hydrochloric acid electrolyte.

### **1. INTRODUCTION**

Production of composites from refractory metals suitable for exploitation in the oxidizing ambient at high temperatures of 1900–2200°C is a promising direction in the development of aerospace engineering. Manufacturing of such materials would enhance the efficiency of the thermocatalytic low-thrust engines by the possible utilization of “green fuels” [1–2]. Nowadays rhenium and its composites are extremely popular in fundamental and applied research [3–9].

The high-temperature electroplating from molten salts of different compositions is a perspective method of rhenium composites formation. In recent years, this method has come to prevail and it has completely replaced such methods as plasma spraying, vacuum condensation and gas-phase transport reaction. The high rate of deposition, possibility of the uniform coating distribution over at the sample surface and low metal losses are major advantages of the high-temperature electroplating method [10].

The rhenium nucleation and generation of continuous homogeneous layer in molten salts is a complicated task. These complications are associated with non-uniform distribution of current and occurrence of the exchange reactions on the more electronegative substrates, which result in the deposition of heterogeneous sediments. It is possible to eliminate the above-mentioned obstacles by the preliminary electrodeposition of a sublayer. In addition, the electrodeposition should be performed at low temperatures under conditions, in which the exchange processes between the metal and electrolyte are complicated and proceed slowly.

Aqueous solutions of rhenium are perspective media for rhenium films electrodeposition. Development of the technique of rhenium films electrodeposition will provide a possibility to obtain high quality Re coatings with the subsequent plating of rhenium in the molten salt media. Rhenium, which is obtained using the aforesaid technique, will have a microcrystalline structure.

The aqueous solutions allow forming rhenium deposits under normal conditions, but the high rates of exchange reactions are not typical for aqueous solutions. Therefore, the rhenium sublayer obtained from the aqueous solution makes the deposit formation more homogeneous. A rhenium film will prevent the occurrence of possible exchange processes.

There is vast published data related to the rhenium cathodic reduction from aqueous solutions [11-19].

In the data available in open sources [12] it is stated that the aqueous alkaline solutions cannot be used for the rhenium electrodeposition, as rhenium deposits in such solutions crystallize in the form of rhenium oxides. *Vargas-Uscategui et al* [15] proved experimentally that the rhenium electrodeposition from the alkaline aqueous  $\text{NH}_4\text{ReO}_4 + \text{NaOH}$  (pH 13.3) solution is a multistage process with a mutual formation of deposits of the following composition  $\text{Re}-\text{ReO}_2-\text{ReO}_3$ .

Zerbino and Schrebler [14, 17] illustrated the possibility of the thin rhenium films formation at golden and platinum electrodes by electrodeposition from the  $\text{Na}_2\text{SO}_4+\text{H}_2\text{SO}_4$  (pH 2) aqueous solution in the presence of  $\text{HReO}_4$ . The experimental results demonstrated that in the region of potentials, which precede the hydrogen evolution reaction, as the rhenium oxide as the metallic rhenium deposits form under the oxide layer in the hydrogen reduction region. The co-reduction of rhenium and its oxides, strong influence of the electric potential on the rhenium deposits behavior, possible side absorption and catalytic reactions and high cost of the process are the minor points of this method.

All reviewed papers related to the rhenium electrodeposition reported on the deposits, which had high oxygen concentrations in the oxide forms. One of the possible reasons is that a high purity metallic rhenium is obtained by the electrolysis of non-aqueous solutions [20] or by the hydrogen reduction [21].

Let us note that in all papers under discussion, the rhenium was added into the solution in the form of water soluble oxide compounds. Such rhenium compounds are likely to co-deposit partially.

The aim of the present work is to prove the possibility of rhenium films formation free of the oxygen containing rhenium compounds in the  $\text{HCl}$  aqueous solutions.

Techniques of the metallic rhenium selective dissolution and the formation of the rhenium chloride solution were investigated. The prepared solution obtained served as an electrolyte. The chemical compositions of the obtained deposits were analyzed.

## 2. EXPERIMENTAL

Rhenium layer was electrochemically obtained in the aqueous solution of hydrochloric acid of the 200-350 g/l concentration containing 0.5-10 g/l of metallic rhenium compounds. High purity hydrochloric acid with the density of 1.185 g/cm<sup>3</sup> with the mass fraction of chlorine hydride of 38% was used for the electrolytes preparation. The rhenium concentration in the solution was set by the preliminary anode dissolution of high purity metallic rhenium with the concentration of 99.98 wt. % rhenium. The preliminary dissolution was performed under galvanostatic conditions at the anode current density of 1 A/cm<sup>2</sup> for 2 hours.

Experiments, aimed for the obtaining the electrolytic rhenium deposits, were performed in the thermostatic two-electrode electrochemical cell. The operating temperature was varied within the range of 25-40 °C. The temperature was maintained using a thermostat Grant Optima T100-ST38.

The cathode current density was designated using an electrochemical station Autolab PGSTAT302N. The electrochemical cell potential was continuously recorded during electrolysis. A nickel plate with concentration of 99.6 wt. % Ni was applied as a forming tool. High purity rhenium with concentration of 99.98 wt. % was utilized as an anode.

The cathode current efficiency was determined after each experiment by the gravimetric method using a Sartorius Secura 124-1ORU weight set. The obtained deposits were analyzed by the XRD, SEM and EDS methods.

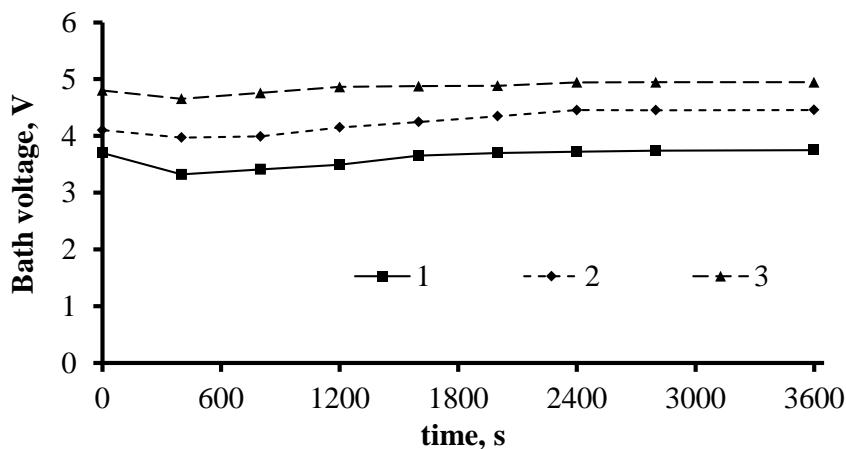
## 3. RESULTS AND DISCUSSION

The electrolysis was performed in a glassy electrochemical cell in galvanostatic regime at the cathode current density ranging from 0.1 to 1 A/cm<sup>2</sup> during 25-55 minutes. The cathode current efficiency was calculated according to the results of each experiment. The results are presented in Table 1.

**Table 1.** Results of the electrolysis

Nº	Re concentration, g/l	i <sub>k</sub> , A/cm <sup>2</sup>	U, V	Substrate	Form of the deposit	Current efficiency, %
1	0.52	0.1	2.712	Ni	Island film	9,6
2	0.94	0.2	3.025	Ni	Clusters	10,3
3	1.63	0.2	3.228	Ni	Solid film	11,5
4	2.43	0.3	3.414	Ni	Solid film	11,9
5	5.92	0.5	3.700	Ni	Solid film	14,6
6	9.87	1.0	4.100	Ni	Solid film	15,0

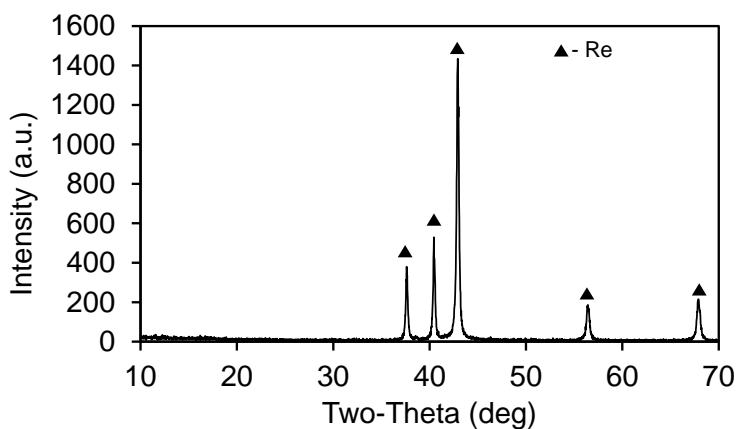
Typical time dependences of voltage at the current density of 0.5 – 1.3 A/cm<sup>2</sup> are presented in Fig. 1.



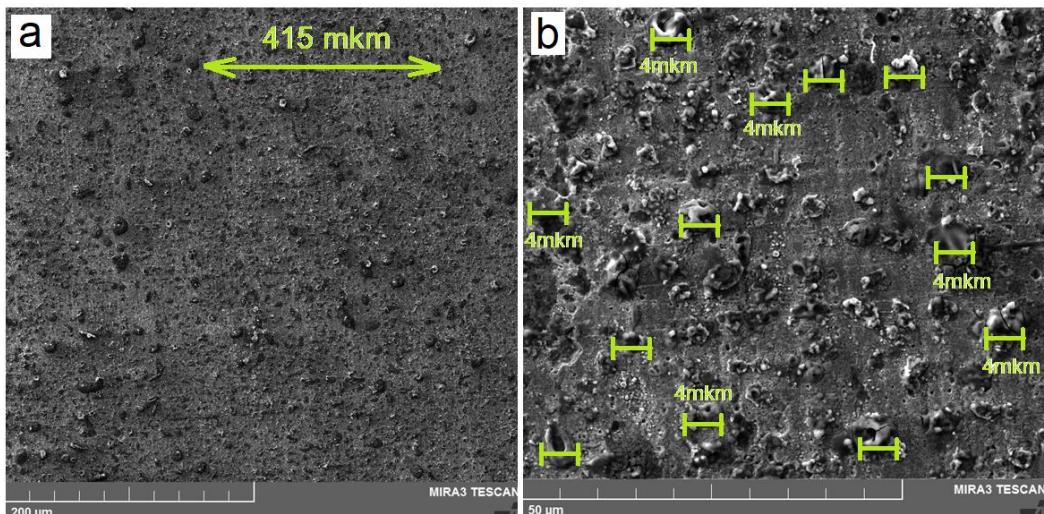
**Figure 1.** Time dependencies of bath voltage at the rhenium electrodeposition on nickel electrode from the 300 g/l HCl solution and 5 g/l metallic Re compounds at the temperature of 40°C and at the cathode current densities: 1 – 0.5 A/cm<sup>2</sup>; 2 – 1.0 A/cm<sup>2</sup>; 3 – 1.3 A/cm<sup>2</sup>

It is illustrated in Fig. 1 that the electrolytic cell potential decreases at the initial moment of electrolysis. Such peculiarity may be explained by the increase in the electrical conductivity of electrolyte, which is associated with the rise in the rhenium ions concentration in the solution. The further increase in rhenium concentration results in the decrease in the electrical conductivity and, therefore, in the increase in the electrolytic cell potential. This dependence is explained by a large size of rhenium ions as compared to those of hydroxonium ions, which are superconductors. In addition active hydrogen evacuation accompanies the rhenium electrodeposition in the water solution, which decreases rhenium current efficiency. Jones [22] presented data regarding the current efficiency during obtainment of rhenium deposits in sulfate and alkali electrolytes. In all tested electrolytes the current efficiency varied within 2 – 15%, which is in agreement with the results obtained in the present work.

The nickel samples with thin rhenium coatings were obtained during the electrodeposition. They were analyzed using the X-ray diffraction, electron scanning microscopy (SEM) and energy disperse X-ray spectroscopy (EDS) methods. The results are given in Figs. 2 and 3.



**Figure 2.** Diffractogram of the rhenium deposit obtained on the nickel substrate in the solution of 350 g/l HCl and 9.87 g/l metallic Re compounds at the temperature of 40°C and at the cathode current density of 1 A/cm<sup>2</sup>

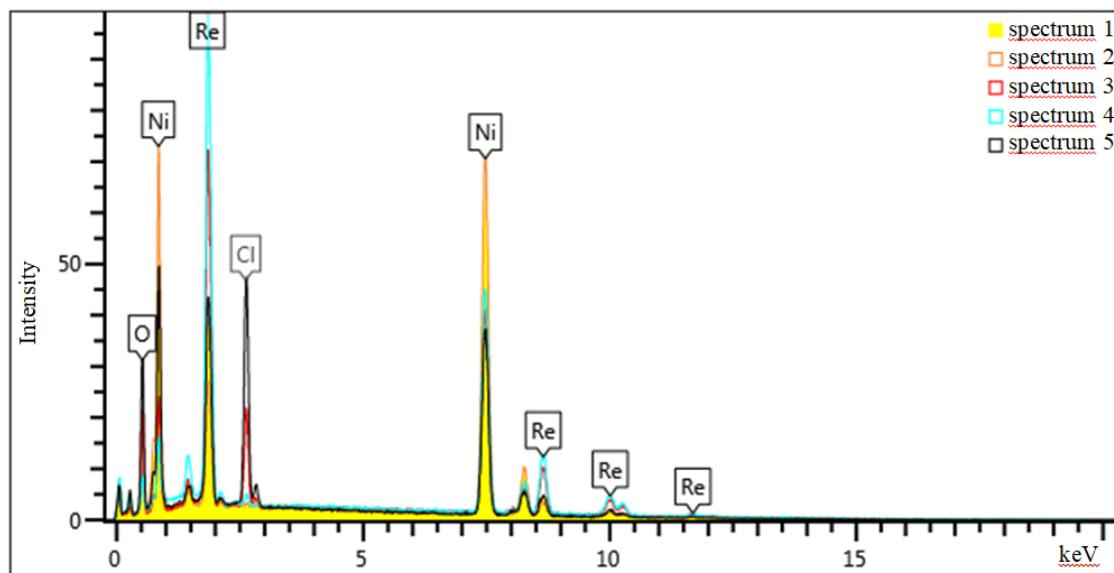


**Figure 3.** SEM images of the electrolytic rhenium deposit obtained on the nickel substrate at the temperature of 40°C and at the cathode current density of 1 A/cm<sup>2</sup>

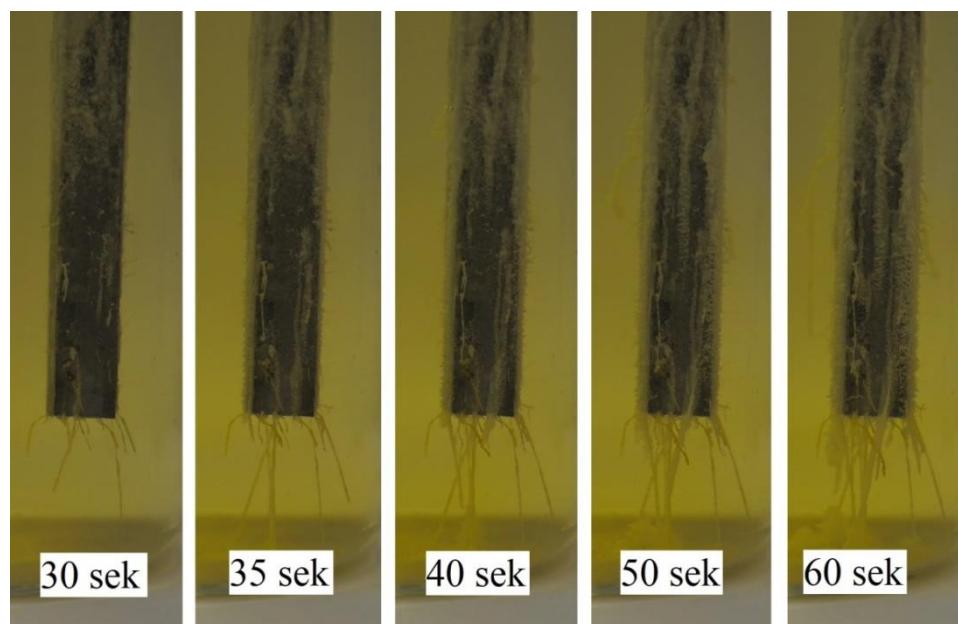
According to the SEM data, the film, which appeared on the surface of the nickel substrate, is formed as the result of the electrolysis. A general shape of the film is typical for electrolytic deposits, formed by the aqueous solutions electrolysis. The film is uniformly spread over the cathode electrode surface. The spots of secondary crystallization, i.e. clusters, were detected (Fig. 3). The average size of the clusters at the secondary crystallization of the rhenium film was 4  $\mu$ m. Almost uniform size of clusters in this case may testify that there is the transfer to the instantaneous nucleation at the film grains boundaries. This fact also states that the film growth (and the further coating growth) proceeds under a marked diffusion control, i.e. during the cluster growth the area, from which the material for the cluster formation is taken, is overlapping with the area, from which the material for a neighboring cluster formation is taken.

Thus, there are enough conditions for the film formation. Moreover, the rhenium sublayer deposition may be performed. An application of the sublayer is a technological solution of the problem. This approach may be used for crystallization of more thick layers in molten salts. The presence of similar phase would bring a positive impact on the structure and morphology of cathode deposits, which are grown on this phase. However, the nucleation process in this case requires a further study by means of electrochemical methods. Determination of the crystallization mechanism and a detailed study of the process will reveal new possibilities for controlling the rhenium sublayer structure.

In the course of the present research we determined the anion, from which the rhenium electrodeposition begins, was determined. The solution of saturated cesium chloride was added into the electrolyte for the rhenium deposition. The cesium chloride concentration was designated within the solubility limits and it was equal to 1500 g/l [23]. The obtained electrolyte was used for the rhenium electrodeposition. During the process we observed the formation of salt deposits on the cathode (Figs. 4, 5).



**Figure 4.** Results of the EDS analysis of the rhenium sublayer obtained from the solution of 350 g/l of HCl and 9.87 g/l of metallic Re compounds at the temperature of 25°C and at the cathode current density of 0.5 A/cm<sup>2</sup>



**Figure 5.** Growth dynamics of the salt deposit on rhenium anode in the solution of 350 g/l of HCl and 9.87 g/l of metallic Re compounds and 1500 g/l of CsCl at the temperature of 25°C and at the anode current density of 1 A/cm<sup>2</sup>

Due to the different values of the current efficiency at the anode and at the cathode, the rhenium-containing ions, which interact with the saturated cesium chloride solution up to the rhenium-containing salt formation according to equation (1), are accumulated.

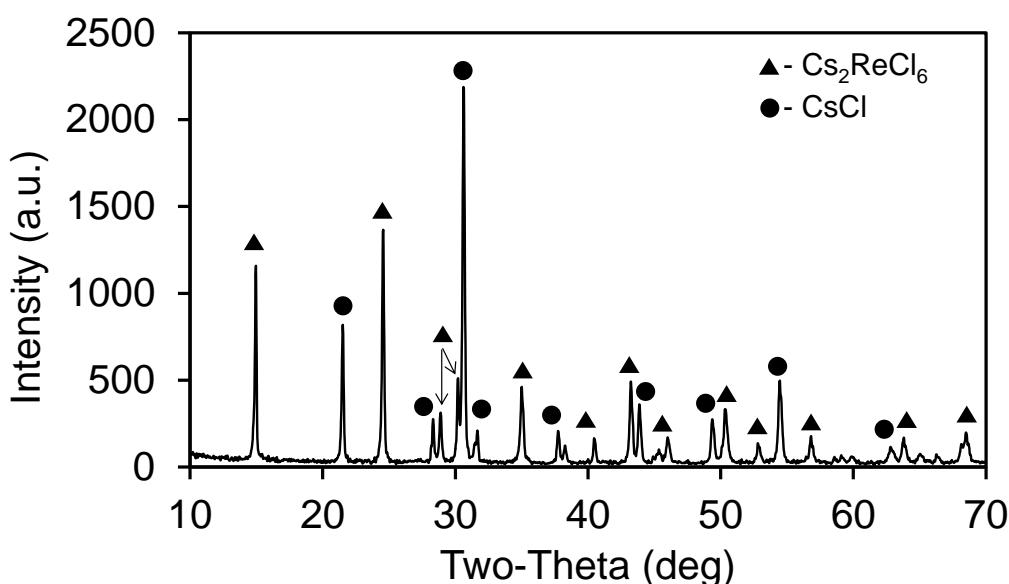


As the concentration reaches the solubility limit of the salt, the salt phase crystallization at the anode is observed. A general view of the anode with the salt deposit is demonstrated in Fig. 6.



**Figure 6.** General view of the rhenium anode covered by the salt deposit, which was obtained at the temperature of 25°C and at the anode current density of 1 A/cm<sup>2</sup>

In order to determine the phase composition of the salt deposit the anode was withdrawn from the solution and it was dried in air. Then, the salt deposit was removed from the anode by a knife and then it was grinded in the agate mortar. The phase composition was determined by the X-ray diffraction method using an automatic X-ray diffractometer Rigaku D/MAX-2200VL/PC. The obtained diffractograms were interpreted by means of the MDI JADE 6.5 program. The results are presented in Fig. 7.



**Figure 7.** Diffractogram of the salt deposit, which was obtained at the temperature of 25°C and at the anode current density of 1 A/cm<sup>2</sup>

The X-ray phase analysis elucidated that the obtained salt deposit did not contain any oxide phases, and therefore, the rhenium discharge at the cathode is originated by the chlorinate anion. This peculiarity has a positive impact on the metallic rhenium crystallization, as opposed to other aqueous solutions. Vargas-Uscategui [15] reported that the rhenium deposits obtained from the alkali water solution are multiphase; besides, they contain rhenium oxides mixtures alongside with metallic rhenium. Szabo [24] also stated that the rhenium deposits could crystallize in the form of oxides with various compositions in the sulfate electrolytes.

#### 4. CONCLUSIONS

Thus, considering the overall data obtained it is possible to conclude that during the electrolytic rhenium deposition from the aqueous solution of hydrochloric acid, which contains rhenium compounds, allows forming a uniform metallic sublayer, i.e. a rhenium film, can be formed. The obtained rhenium film may be utilized for the further rhenium deposition in different media including molten salts.

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