Influence of electrolysis mode, complex formation and micropassivation on the roughness of niobium and tantalum coatings

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Abstract. It is shown that the use of pulsed electrolysis has significant advantages compared with the stationary mode and allows obtaining coatings with a lower level of roughness. The effect of complex formation on the quality of niobium and tantalum coatings is discussed. The effect of micropassivation on the roughness of niobium coatings obtained by the electrolysis of molten salt based on an equimolar mixture of sodium and potassium chlorides has been established.

1. Introduction
Niobium and tantalum have an exceptional corrosion resistance in various corrosive media [1]. Extreme conditions of articles exploitation cause utilization of expensive refractory metals ensuring their adequate performance. The problem can be approached by depositing coatings on the surface of units and mechanisms, i.e. creating composite materials. In this case, the substrate material provides the strength and electric characteristics while the coatings realize the necessary surface properties, including corrosion resistance. In each particular case, coating techniques should be selected taking into account the expected service conditions of the coating. Nowadays coatings are mostly produced by CVD, PVD methods, plasma and detonation spraying. A promising method for the production of niobium and tantalum coatings is electrodeposition from molten salts [2–7].

Electrodeposition of niobium (tantalum) coatings using molten salts has the following advantages in comparison to other methods [7]:
- melt electrolysis using pulse and reverse current provides the possibility to easily control the deposit structure, thickness, porosity, degree of roughness, texture of galvanic coatings, and grain size (up to nanosized values);
- electrodeposition parameters determined on laboratory installations can be scaled to large ones and adjusted to processes using substrates of complex shapes with control of the thickness, grain size, and composition of coatings;
- high purity of the obtained coatings even when using low quality initial reagents;
- low costs of operation and electrochemical equipment.

The goal of this study was the electroplating of niobium and tantalum coatings using stationary and pulsed electrolysis modes, studying the effect of complex formation and micropassivation on the roughness of coatings.
2. Experimental

For electrodeposition of niobium coatings were used electrolyte on the base of equimolar mixture NaCl-KCl containing 8 wt. % $K_2NbF_7$ and 10 wt. % NaF (I) and the CsCl-CsF(10 wt. %)-$K_2TaF_7$ (8 wt. %) (II). The molten salt systems NaCl-KCl-NaF (10 wt. %)-$K_2TaF_7$ (10 wt. %), (III) and CsCl-CsF (10 wt. %)-$CsTaF_6$ (10 wt. %) (IV) were utilized for deposition of tantalum coatings.

Alkali chlorides (NaCl, KCl, CsCl) were purchased from Prolabo (99.5 % min.). They were dehydrated by continuous and progressive heating just above the melting point under gaseous HCl atmosphere in quartz ampoules. Excess HCl was removed from the melt by argon. The salts were handled in the glove box and stored in sealed glass ampoules. Sodium and cesium fluorides (Aldrich 99.5 % min.) was purified by double melt recrystallization: NaF and CsF were dried in a glassy carbon crucible (SU-2000) at 673–773 K under vacuum, then heated up to a temperature 50 K above its melting point and finally cooled down 50 K below the melting point at a rate of 3–4 K per hour. The solidified salts were transferred at 393 K to a dry glove box and impurities were removed mechanically. The procedures of preparation of alkali halide salts described in [7].

Potassium heptafluoronioobate and heptafluorotantalate were prepared by recrystallization of extra pure salt (content of metallic impurities of $10^{-3}$ wt. %; manufactured by the workshop of the Tananaev Institute of Chemistry) from hydrofluoric acid solutions followed by washing with ethanol and drying in a vacuum oven at 383–393 K.

Hexafluoroniobate and hexafluorotantalate were obtained by dissolving niobium hydroxide and tantalum in “chemically pure” 40% hydrofluoric acid in Teflon vessel, and a saturated aqueous solution of cesium chloride was added to the obtaining solution in a strictly stoichiometric ratio. The precipitate was subjected to recrystallization in HF (1:1), filtered on a suction filter, washed with alcohol and dried under vacuum at a temperature of 373 K.

The voltammetric curves were recorded on tungsten and copper electrodes with diameters of 0.8–2.0 mm relatively to a SU-2000 glassy carbon or platinum quasi-reference electrodes. The tungsten and copper do not form intermetallic compounds with niobium and tantalum and their solubility in these metals is low. While the potential of this quasi-reference electrode does not constitute a thermodynamic reference, the use of this electrode was preferred in order to avoid any contact between the melt and oxygen-containing material as used in classical reference electrodes. The potential sweep rate ($\nu$) was varied from $5 \times 10^{-3}$ to 2.0 V s$^{-1}$.

All the experiments concerned with the electrochemical behavior of niobium, tantalum complexes and deposition of niobium (tantalum) coatings were carried out at 1023 K.

The salt mixture prepared by the above-described procedure was placed in a niobium (tantalum)-lined molybdenum crucible and transferred to the retort of the electrolytic cell. The design of the cell was described in detail earlier [8]. The electrolyte in the cell retort was evacuated to a residual pressure of 3 Pa at 120 °C, the cell was filled with high-purity grade argon, which was passed through the LLC “SOLO” SOG-4 gas purification system and the electrolyte was melted.

The anodic current density was less than $1 \times 10^{-5}$ A cm$^{-2}$, the cathodic current density in galvanostatic electrolysis varied within the range $5 \times 10^{-5}$–$1 \times 10^{-1}$ A cm$^{-2}$. In pulsed electrolysis, the direct current pulses of $1 \times 10^{-2}$–$2 \times 10^{-1}$ A cm$^{-2}$ were alternated with pauses. The ratio between the current pulse width ($t_{el}$) and the pause duration ($t_{p}$) was varied in a wide range: $t_{el}=0.5$–5 s, $t_{p}=1$–5 s.

To optimize the coating electrodeposition parameters, we chose the following criteria: current efficiency by the metal deposited into a coating and roughness $R_d$ (arithmetic mean of profile deviations). Such a criterion as the current efficiency by the metal deposited into a coating is used because not only a coating is formed in electrodeposition, but, occasionally, also dendrites lost in washing to remove the electrolyte.

To identify the cathodic products, a Shimadzu XRD-6000 diffractometer (Shimadzu, Kyoto, Japan) was used. The roughness of niobium (tantalum) coatings was determined with a profilometer Profi-130 (Russia).
3. Results and discussion

Electrochemical behavior of niobium was studied in detail [9]. It was shown that the discharge of oxofluoride (oxygen-containing) complexes in the NaCl-KCl-NaF melt precedes the discharge of fluoride (oxygen-free) complexes, which accounts for a more profound transition of oxygen into the cathodic products in the course of electrolysis in this system. In KCl and CsCl melts, the reduction potentials are inverted and oxofluoroniobate complexes discharge at more negative potentials than fluoride complexes.

Figure 1 shows the voltammetric curve of the NaCl-KCl-NaF(10 wt. %)-K_2TaF_7 melt obtained on a copper electrode. When oxygen anions are introduced into the NaCl-KCl-NaF(10 wt. %)-K_2TaF_7 melt (figure 2), wave R_1, which is responsible for the discharge of TaF_7^2- complexes to the metal decreases in the voltammetric curve. The wave of the electroreduction oxofluoride complexes, which discharge at more negative potentials than fluoride complexes increases (figure 2). The voltammogram only has wave R_2 without wave R_1 at a molar ratio O_2^-/TaF_7^2-=1:1. This transformation of the voltammetric curve and the transition to peak II is explained by the interaction:

$$TaF_7^{2-} + O_2^- \leftrightarrow TaOF_6^{3-} + F^-$$  \hspace{1cm} (1)

**Figure 1.** The cyclic voltammetric curve obtained in the NaCl-KCl-NaF (10 wt. %)-K_2TaF_7 melt on a copper electrode. C(K_2TaF_7)=7.31 \times 10^{-5} \text{ mol cm}^{-3}; \nu = 0.5 \text{ V s}^{-1}; T=1023 \text{ K}; \text{ Pt-quasi reference electrode.}

**Figure 2.** Cyclic voltammogram obtained in the NaCl-KCl-NaF(10 wt. %)-K_2TaF_7 melt on a copper electrode. \nu =1.0 \text{ V s}^{-1}; T=1023 \text{ K}; C(K_2TaF_7)=6.23 \times 10^{-5} \text{ mol cm}^{-3}; C(Na_2O)=1.36 \times 10^{-5} \text{ mol cm}^{-3}. GC-quasi reference electrode.

In melts on the base KCl and CsCl also oxofluoride complexes of tantalum discharge at more negative potentials than fluoride complexes.
The results were taken into consideration if the current efficiency by the metal deposited into a coating exceeded 90% and the coating thicknesses differing by 1–2 μm, which enables a correct analysis of the coatings roughness. Selected results obtained in deposition of niobium and tantalum coatings are listed in tables 1 and 2. As can be seen from the tables 1 and 2, the pulsed electrolysis makes it possible to obtain coatings with lower roughness, compared with the galvanostatic mode.

Analyzing the obtained results, it should be noted that the roughness of coatings for the melt I is lower than for the melt II. It could be assumed that the use of the CsCl-CsF-CsNbF₆ salt system will lead to the emergence of a larger number of crystallization centers and a reduction in roughness compared to the NaCl-KCl-NaF-K₂NbF₇ salt system. Since niobium complexes have a greater strength and lower values of diffusion coefficients in the salt system (II) [10, 11]. However, the number of crystallization centers formed is seriously affected by the micropassivation phenomenon [12]. Passivators in the melt (I) can be niobium oxides and suboxides [13–14], since the monooxo-fluoride complexes of niobium in the melt (I) are discharged at more positive potentials than fluoride complexes [9]. The effect of micropassivation leads to the splitting of large crystals with the formation of a plurality of crystallization centers, which makes it possible to obtain coatings with a low level of roughness. The phenomenon of micropassivation in the melt (II) was not observed, since in this melt the monooxo-fluoride complexes have a more negative discharge potential than fluoride complexes. Thus, during the electrodeposition of niobium coatings from the melt based on sodium and potassium halides, the micropassivation effect prevails over complex formation.

Table 1. The values of the roughness niobium coatings obtained from different electrolytes under dissimilar electrolysis regimes.

| \(i_c\), A cm\(^{-2}\) | \(t_{el}\), s | \(t_{p}\), s | \(R_a\), \(\mu m\) |
|-----------------|-------------|-------------|----------------|
|                 |             |             | NaCl-KCl-NaF  | CsCl-CsF |
| 0.05            | -           | -           | 1.22          | 1.78 |
| 0.05            | 0.5         | 2           | 0.89          | 1.03 |
| 0.05            | 1           | 1           | 0.39          | 1.43 |
| 0.1             | 0.5         | 1           | 0.52          | 1.62 |
| 0.1             | 1           | 1           | 0.50          | 1.39 |
| 0.1             | 5           | 2           | 0.80          | 0.98 |
| 0.2             | 5           | 5           | 0.58          | 1.37 |

In molten salts (III) and (IV), tantalum oxofluoride complexes are discharged at more negative potentials than fluoride [3]. In this case, during the electrodeposition of tantalum coatings, one should not expect micropassivation of the cathode sediment with oxygen-containing impurities, and “a priori” it can be assumed that if the composition of the second coordination sphere changes from sodium to cesium, the coatings will have a lower level of roughness.

Table 2. The values of roughness tantalum coatings obtained from different electrolytes under dissimilar electrolysis regimes.

| \(i_c\), A cm\(^{-2}\) | \(t_{el}\), s | \(t_{p}\), s | \(R_a\), \(\mu m\) |
|-----------------|-------------|-------------|----------------|
|                 |             |             | NaCl-KCl-NaF  | CsCl-CsF |
| 0.05            | -           | -           | 1.14          | 0.91 |
| 0.05            | 0.5         | 2           | 0.72          | 0.52 |
| 0.05            | 1           | 1           | 0.61          | 0.41 |
| 0.1             | 0.5         | 1           | 0.50          | 0.38 |
| 0.1             | 1           | 1           | 0.50          | 2.23 |
| 0.1             | 5           | 2           | 0.74          | 0.68 |
| 0.2             | 5           | 5           | 0.64          | 0.58 |
| 0.2             | 0.5         | 2           | 0.54          | 0.35 |
Indeed, when using all modes of electrolysis, the roughness level in the melt based on the CsCl was lower than in the melt based on the equimolar mixture NaCl-KCl.

4. Conclusion
Regarding the level of roughness of niobium and tantalum coatings, in melts based on the NaCl-KCl-NaF melt, \( R_a \) had similar values due to the effect of micropassivation in a system with niobium. For melts containing in the second coordination sphere cesium cations, the roughness of the tantalum coatings was less than that of niobium. The decrease in \( R_a \) of the tantalum coatings is explained by the greater strength of the fluoride complexes of tantalum in comparison with the fluoride complexes of niobium. This is indicated by more negative discharge potentials of tantalum complexes and lower exchange currents [14].

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