Obtaining powders and coatings of various tantalum silicides by electrochemical methods

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Abstract. Joint electroreduction of tantalum and silicon fluoride complexes was studied by cyclic voltammetry in the (NaCl-KCl)equimol.-NaF-K2SiF6-K2TaF7 melt. The formation of tantalum silicides has been studied by cyclic voltammetry and chronopotentiometry methods. Parameters for electrochemical synthesis of tantalum silicides were found. Tantalum silicide powders were obtained by potentiostatic electrolysis at different potentials, at temperature of 1073K and duration of the process 2 hours. Tantalum silicide coatings on a silver substrate were synthesized by galvanostatic electrolysis at current densities 30–130 mA cm−2 and contact displacement method. The relationship between current density and composition of the tantalum silicide coatings was shown.

1. Introduction
Refractory metal silicides are widely used in the modern techniques. For example, they can be used for protection against the high-temperature oxidation of the refractory metals and their alloys [1], utilized in different electronic devices [2–4]. Direct synthesis from elements or reduction of there were used for the synthesis of tantalum silicides [1].

At the same time, refractory metal silicides can be obtained by high-temperature electrochemical synthesis in molten salts [5, 6].

In electrochemical synthesis, the formation of compounds is realized at the atomic level, that allow to carry out the process at low temperatures 1073–1123 K. Pulse electrolysis and reverse electrolysis of molten salts provide the ability to easily control the structure of deposits, thickness, porosity, roughness, texture and crystal size.

The aim of this work is the determination of the electrochemical synthesis parameters for obtaining tantalum silicides powders and coatings in chloride-fluoride melts.

2. Experimental
The technique of the salt preparation consists of the following. Sodium and potassium chlorides of “pure grade” were subjected to recrystallization, tempered in a muffle furnace, mixed in an equimolar ratio, and placed into a quartz retort. The retort was evacuated to a vacuum of 0.66 Pa firstly at room temperature and next heated at gradually rising steps to 473, 673, 873 K. After that it was filled by argon and the electrolyte was melted.

NaF, K2TaF7 and K2SiF6 of “reagent grade” were used without additional treatment.
The background molten salts were placed into a glassy carbon crucible of grade SU 2000 and charged into the retort of an electrochemical cell of stainless steel, where the abovementioned operations of vacuuming and melting were repeated.

Electrochemical studies were performed in the temperature range of 973–1073 K by cyclic voltammetry method using an AUTOLAB PGSTAT 20 potentiostat. Potential sweep rate (v) was varied in the range of 0.2 to 2.0 V s\(^{-1}\). A glassy carbon crucible served as the auxiliary electrode. Voltammetric curves were recorded on a Ag electrode vs. a Pt quasi-reference electrode.

To study the formation of tantalum silicides a chronopotentiometry method was utilized. An equimol mixture of NaCl-KCl containing 10 wt.% of NaF and 2.0–5.0 wt. % K\(_2\)TaF\(_7\) was used as electrolyte being in contact with metallic tantalum [5].

Working electrode of silicon plate was degreased in ethyl alcohol with the use of ultrason. A glassy carbon crucible was used as an auxiliary electrode. As a reference electrode, we used metallic tantalum deposited by galvanostatic electrolysis (current density of 0.2 A cm\(^{-2}\), temperature of 1023 K, electrolysis duration of 10 min) on a molybdenum bar.

Charging curves (cathodic chronopotentiograms) were recorded at a temperature of 1023 K and a current density of 3 \(10^{-3}\) A cm\(^{-2}\) until the potential difference of the cathode and the reference electrode of tantalum become zero. After that, the electrolytic cell was switched off and the open-circuit chronopotentiogram (OCP) was recorded. The preference was given to recording the OCP because they had better reproducibility than cathodic chronopotentiograms [7].

To identify the cathodic products the diffractometer DRON-2 with monochromatic Cu\(_{Kα}\) radiation and a scan rate of 0.25 deg per min was used. Macrostructure of tantalum silicides was investigated using microscope Axio Observer D1m «Carl Zeiss» with «Thixomet» image analyzer.

### 3. Results and discussion

On the cyclic voltammogram of the melt (NaCl-KCl\(_{\text{eqimol.}}\)-NaF (10 wt.%), K\(_2\)SiF\(_6\) in the cathode semi cycle present two electroreduction peaks R\(_1\) and R\(_2\) for Si(IV) complexes. However, an increase in the K\(_2\)SiF\(_6\) concentration resulted in the fact that the first reduction wave was characterized by a barely noticeable inflection or that no visible wave resolution was observed in the case of the cathodic polarization [8]. At the same time, silicon electrooxidation peaks O\(_1\) and O\(_2\) were always clearly pronounced in the anodic semi cycle of the voltammogram. It is established that the electroreduction of silicon proceeds in two stages [8]:

\[
\begin{align*}
\text{Si(IV)} + 2e & \rightarrow \text{Si(II)} \quad (1) \\
2\text{Si(II)} & \leftrightarrow \text{Si(IV)} + \text{Si} \quad (2) \\
\text{Si(II)} + 2e & \rightarrow \text{Si} \quad (3)
\end{align*}
\]

Stage (1) was reversible in a wide range of the rate of polarization, but at \(v \leq 0.5\) V s\(^{-1}\) it is complicated by the disproportionation reaction (2). The second stage (3) is quasi-reversible to \(v < 2.0\) V s\(^{-1}\), and with \(v \geq 2.0\) V s\(^{-1}\) becomes irreversible [8].

The cyclic voltammogram of the melt (NaCl-KCl\(_{\text{eqimol.}}\)-NaF (10 wt.%), K\(_2\)TaF\(_7\), is characterized by one peak of electroreduction in the cathodic semi cycle and a peak of electro-oxidation in the anodic semi cycle. Using potentiostatic electrolysis at potentials corresponding to the cathodic peak, according to X-ray diffraction data, metallic tantalum was obtained at the cathode, which allows one to make a conclusion about the one-stage discharge of TaF\(_2^+\) complexes by the reaction [9]

\[
\text{TaF}_{2^+} + 5e \rightarrow \text{Ta} + 7\text{F} \quad (4)
\]

Based on the diagnostic criteria of the cyclic voltammetry method, the process of discharging fluoride tantalum complexes to metal (4) is classified as irreversible, that is, controlled by the rate of charge transfer. This conclusion is in accordance with the results of [10–11], in which the electroreduction of tantalum complexes in chloride and fluoride – chloride melts was studied.

Joint electroreduction of tantalum and silicon complexes was investigated by cyclic voltammetry. The five cathodic peaks on the voltammogram were registered in the (NaCl-KCl\(_{\text{eqimol.}}\)-NaF-K\(_2\)SiF\(_6\), K\(_2\)TaF\(_7\) melt (figure 1). Four cathodic peaks (R\(_2\), R\(_3\), R\(_4\) and R\(_5\)) probably correspond to the formation of tantalum silicides according to Ta-Si equilibrium phase diagram and the fifth peak (R\(_1\)) – to the
silicon electrodeposition. Potentiostatic electrolysis was used to identify these peaks. The phase composition of the cathodic products is given in the table 1.

![Cyclic voltammogram of the melt (NaCl-KCl)equimol.-NaF (10 wt. %)-K₂SiF₆-K₂TaF₇, v = 1.0 V s⁻¹, T = 1073 K, C(K₂SiF₆) = 1.954 10⁻⁴ mol cm⁻³, Ta:Si = 1:1. Quasi-reference electrode – Pt.](image1)

At the same time, the open-circuit chronopotentiogram, recorded on silicon electrode (figure 2) shows five plateaus of the potential delay (a, b, c, d, e), which, according to the equilibrium state diagram of tantalum-silicon [12], correspond formation of two-phase regions Ta₃Si + Ta, Ta₃Si + Ta₂Si, Ta₂Si + Ta₅Si₂, Ta₅Si₂ + Si in the surface layer, respectively. Potentiostatic electrolysis at plateau potentials (figure 2) resulted in the formation of cathodic deposits with the following composition: at the potential corresponding to plateau “a” – a mixture of metal tantalum and tantalum silicide Ta₃Si, plateau “b” – silicides with composition Ta₂Si + Ta₃Si, plateau “c” – a two-phase product of silicides Ta₂Si + Ta₅Si₂, at potential "d" – a mixture of silicides Ta₅Si₂ + Ta₁Si₂ and at potential "e" – tantalum silicide composition TaSi₂ + Si.

![OCP of the melt (NaCl-KCl)equimol.-NaF (10 wt. %)-K₂TaF₇, T = 1073 K, C(K₂SiF₆) = 1.954 10⁻⁴ mol cm⁻³, Ta:Si = 1:1. Quasi-reference electrode – Ta.](image2)

Potentiostatic electrolysis in all cases led to the deposition of tantalum silicide powders on the cathode. Tantalum silicide coatings on a silver substrate were deposited using galvanostatic electrolysis in the melt (NaCl-KCl)equimol.-NaF-K₂SiF₆-K₂TaF₇. Electrolysis time – 3 hours, temperature – 1073 K, concentration of K₂SiF₆ was 5.092 10⁻⁴ mol cm⁻³, mole ratio Ta:Si – 1:1. The phase composition of the cathodic products is given in the table.

The morphology of the powders and coatings was investigated by optical microscopy (figure 3). The sizes of individual particles of Ta₃Si powder are 800–900 nm, while these particles form agglomerates with sizes of 10–20 μm (figure 3(a)). The structure of the coatings deposited using galvanostatic electrolysis at different current densities is shown in Figures 3(b), (c), (d). The coating obtained at a current density of 30 mA cm⁻² (figure 3(b)) is two-phase and is a mixture of TaSi₂ and Si. This composition has a developed surface and consists of elongated crystals with a length of about 20–30 microns with a cross section of 1–3 microns. The Ta₅Si₂ (c) and Ta₃Si (d) coatings, synthesized
at cathodic current densities of 80 and 90 mA cm$^{-2}$, respectively, are solid, have a thickness of about 8 μm, and repeat the texture of the surface of the original substrate.

![Figure 3](image1.png)

**Figure 3.** Morphology: (a) – powder of Ta$_3$Si; and tantalum silicide coatings on a silver substrate; (b) – TaSi$_2$+Si (j = 30 mA cm$^{-2}$); (c) – Ta$_5$Si$_3$ (j = 80 mA cm$^{-2}$); (d) – Ta$_3$Si (j = 90 mA cm$^{-2}$).

**Table 1.** Parameters of electrochemical synthesis of tantalum silicide powders and coatings.

| Potential E (vs. Pt), V | Current density -j, mA cm$^{-2}$ | Composition of the cathodic products |
|------------------------|-----------------------------------|--------------------------------------|
| -2.1                   | -                                 | powder Ta$_3$Si                        |
| -1.6                   | -                                 | powder Ta$_3$Si + Ta$_2$Si            |
| -1.2                   | -                                 | powder Ta$_5$Si$_3$ + Ta$_2$Si        |
| -0.8                   | -                                 | powder TaSi$_3$ + Si                  |
| -                     | 30.0                              | coating TaSi$_2$ + Si                 |
| -                     | 50.0                              | coating TaSi$_2$                       |
| -                     | 80.0                              | coating Ta$_5$Si$_3$                   |
| -                     | 90.0                              | coating Ta$_2$Si                       |
| -                     | 110.0                             | coating Ta$_3$Si                      |
| -                     | 130.0                             | coating Ta$_3$Si + Ta                 |

Thermodynamic properties of tantalum silicides was calculated by using the method described in [13]. In a homogenous Ta-Si binary phase with x composition percentage of Ta, the formation equation can be expressed as follows [13]:

$$\text{Ta}_x\text{Si} \leftrightarrow \text{Si} + x\text{Ta}$$  \hfill (5)

The Gibbs formation energy of Ta$_x$Si can be calculated according to the reversible electromotive force ($E'$):

$$\Delta G(\text{Ta}_x\text{Si}) = nxFE'(x) = -RT \ln a_{\text{Ta in Ta}_x\text{Si}}$$  \hfill (6)

On the other hand, for a heterogeneous Ta-Si binary phase system on the silicon electrode, the coexisting state of two intermetallic compounds transferring to each other can be formulated as the following equilibrium equation:
Ta$_x$Si ↔ Ta$_{x-1}$Si + (x1-x2)Si \hspace{1cm} (7)

The electromotive force was in accordance with the plateaus in the OCP curves which are applied to evaluate the Gibbs formation energy of Ta$_x$Si$_y$ silicides:

\[ \Delta E'(x) = -\frac{RT}{n(x_1-x_2)F} \ln \frac{a_{Ta \text{ in } Ta_xSi}}{a_{Ta \text{ in } Ta_{x-1}Si}} \] \hspace{1cm} (8)

Combining (6) and (8), the relationship of Gibbs formation energies between one Ta$_x$Si$_y$ silicide and another for a binary phase equilibrium can be deduced as:

\[ \Delta G_{Ta_{x-1}Si} = \Delta G_{Ta_xSi} - nF \int_{x_2}^{x_1} \Delta E'(x) \, dx \hspace{1cm} (9) \]

The results of the thermodynamic calculations were presented in table 2. They were in a good agreement with experimental data in [12].

**Table 2.** The Gibbs energy of tantalum silicides formation at 1073K.

| Phase   | $\Delta G$, kJ mol$^{-1}$ |
|---------|---------------------------|
| Ta$_3$Si | -43.66                    |
| Ta$_2$Si | -49.21                    |
| Ta$_5$Si$_3$ | -50.65                |
| TaSi$_2$ | -45.83                    |

Tantalum silicides coatings on the tantalum substrates were also obtained by contact displacement.

**4. Conclusion**

The composition of the tantalum silicides coatings depends on the duration and temperature of the process. For example, the formation of Ta$_5$Si$_3$ coatings on Ta substrate by contact displacement can be described by the reaction:

\[ 37Ta + 15K_2SiF_6 \rightarrow 5Ta_5Si_3 + 12K_2TaF_7 + 6KF \hspace{1cm} (10) \]

By varying the time of the process, tantalum silicide coatings of different composition were synthesized.

**References**

[1] Samsonov G and Vinickiy M 1976 *Refractory compounds* (Moscow: Metallurgy)
[2] Murarka S and Chang C 1980 *Appl. Phys. Lett.* 37 639
[3] Kircher C, Mayer J, Tu K and Ziegler J 1973 *Appl. Phys. Lett.* 22 81
[4] So F, Lien C and Nicolet M 1985 *J. Vac. Sci. Technol.* A3 2284
[5] Stulov Y, Dolmatov V, Dubrovskiy A and Kuznetsov S 2016 *Int. J. Electrochem. Sci.* 12 5174
[6] Stern K and Williams C 1986 *J. Electrochem. Soc.* 133 2157
[7] Stulov Y, Dolmatov V, Dubrovskiy A and Kuznetsov S 2016 *ECS Trans.* 75 5174
[8] Kuznetsova S, Dolmatov V and Kuznetsov S 2009 *Russ. J. Electrochem.* 45 797
[9] Marenkova E, Shamshurin A and Kuznetsov S 2015 *Russ. J. Appl. Chem.* 88 132
[10] Konstantinov V 1978 *Electrochim. Acta.* 23 713
[11] Kuznetsov S and Glagolevskaya A 1994 *Russ. J. Appl. Chem.* 67 1093
[12] Schlesinger M 1994 *J. Ph. Equil.* 15 90
[13] Liu K, Liu Y, Yong Yuan L and Wang L 2015 *Electrochim. Acta.* 174 15