

Electrode and chemical reactions during electrodeposition of tantalum products in CsCl melt

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Abstract

This work was accomplished in the context of systematic examination of a role played by electrolyte cation composition in electroreduction processes. The electrochemical behaviour of molten salts systems where CsCl was used as solvent for potassium and caesium oxyfluorotantalates was investigated. In particular, the influence of the electrolysis parameters, such as concentration of tantalum species in electrolyte, temperature and current density on the cathodic products phase composition was determined by X-ray diffraction and scanning electron microscopy. Several phases generally crystallized at the cathode simultaneously. Among identified phases were metallic tantalum in cubic (α) and tetragonal (β) crystal modifications and TaO. But the most characteristic phases for the melt under study were two isostructural compounds with pyrochlor type crystal lattice $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ and $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$. The former deposited in the form of transparent dielectric crystals and the later – in the form of metal-like conductive ones. This latter compound seems to be synthesized for the first time. The peculiarities of its structure were described. Electrochemical redox processes in melts containing potassium oxyfluorotantalates dissolved in CsCl were studied by cyclic voltammetry. Three discharge peaks were detected on voltammograms in the temperature range 700–850 °C. They were associated with the discharge of TaOF_6^{3-} and $\text{TaO}_2\text{F}_4^{3-}$ complexes and alkali metal cations.

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1. Introduction

Electrolysis of a simple molten system containing a halide of refractory metal and an alkali metal halides mixture results in cathodic deposition of refractory metal in a very wide range of electrolysis parameters. Such systems are utilized usually for the electrochemical refining of these metals.

If the electrolysis is performed using more complex systems such as ones including oxygen-containing complex ions, the deposition of a great variety of compounds is possible [1–4]. The phase composition of cathode products may be controlled

in this case by varying parameters of the electrochemical process, such as: temperature, current density, chemical form and concentration of basic metal species, anion and cation composition of solvent. The influence of all these parameters with the exception of the latter on the mechanism of electrochemical processes has been adequately covered in the literature [4].

As for the solvent cation composition its role in electrochemical processes remained out of the focus. This may explain the limited and often nonfunctional choice of solvent employed in electrochemical researches, most of the time the equimolar KCl–NaCl mixture or the ternary LiF–NaF–KF eutectic (FLI–NAK). However, in many cases such a simplified approach to the choice of a solvent selection restricts the amount of information that could be obtained from electrochemical studies. From electrochemical point of view of the above-listed salt systems are essentially mixtures of several halides in random

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combination. Their using removes the possibility to determine the specific role played by each outer-sphere cation of the solvent in an electrochemical process. Meanwhile, our study of niobium-containing salt systems [5,6] showed that this role may be very important and even decisive. It was demonstrated that varying the outer-sphere cation composition is a powerful tool to control the chemical and phase composition of electrolysis products. Thus, only the substitution of sodium for a larger cation (K^+ , for example) in the fluoride solvent for K_2NbOF_5 , other condition being invariable, entailed the oxygen content in the cathodic deposit to be decreased from 14 to 16 wt.% to hundredths of one percent, while their phase composition changed from NbO to pure Nb metal [7]. There is a possibility to synthesize novel low valence niobium compounds with layered structures when KF and RbF melts are used as solvent, but similar phases could not be obtained with LiF, NaF or CsF as solvents.

One might expect that in tantalum-containing oxyhalide melts outer-sphere cations would play also an important role, because Nb and Ta are chemical analogues. This was demonstrated previously in [8]. The present work is the first part of a systematic study of cation composition effect on the electrolysis mechanism in tantalum oxyfluoride–chloride and oxyfluoride–fluoride melts. It is devoted to the electrochemical behaviour of molten salt systems where CsCl is used as solvent for tantalum oxyfluoride complexes.

2. Experimental

Potassium and caesium heptafluorotantalates K_2TaF_7 and Cs_2TaF_7 , potassium and caesium monooxyfluorotantalates K_3TaOF_6 and Cs_3TaOF_6 , potassium dioxyfluorotantalate $K_3TaO_2F_4$ were used as tantalum-containing components of electrolytes. To produce these salts, high-purity tantalum pentoxide, prepared in the laboratory by calcination of electrolytically refined tantalum metal in air at $1100^\circ C$, was dissolved in chemically pure 50 wt.% hydrofluoric acid in a teflon vessel. The precipitation of K_2TaF_7 or Cs_2TaF_7 was initiated by addition of a saturated solution of potassium or caesium fluorides, respectively, at $80^\circ C$. The product was filtered, washed with rectified ethanol and dried under vacuum at $60^\circ C$. K_3TaOF_6 , Cs_3TaOF_6 and $K_3TaO_2F_4$ synthesis were performed by melting K_2TaF_7 or Cs_2TaF_7 , Ta_2O_5 and KF or CsF in appropriate ratios in a glassy carbon vessel under argon atmosphere.

“Spectrally” pure caesium chloride was used. To remove any residual moisture, the salt was heated under vacuum (2 Torr) with a slow stepwise temperature increase up to $500^\circ C$, and then melted in a platinum crucible under argon. Caesium fluoride was prepared from commercial $CsHF_2$ (“chemically pure”) by removal of HF at $600^\circ C$ under argon atmosphere in a platinum crucible.

Voltammetric studies were conducted in a three-electrode cell using a VoltaLab-40 potentiostat with packaged software “VoltaMaster 4 version 6”. The potential scan rate was varied between 50 and 300 mV s^{-1} . The container for the melt was a glassy carbon (GC) ampoule (type SU-2000), which played the role of auxiliary electrode simultaneously, potentials were

measured versus the GC quasi-reference electrode. It is difficult to find the suitable reference electrode for chloride–oxyfluoride melts because of the corrosion action on glass or ceramics used as containers or diaphragms in construction of the traditional reference electrode. In this study that to avoid these difficulties a glassy carbon rod was used. The GC electrode monitors the redox potential of the melt, which remains constant, when composition of the melt is not changed. This potential was not defined thermodynamically, but due to GC quasi-reference electrode during experiments there was no contact between the melt and oxide materials. To obtain more reliable potentials values a Ag/NaCl–KCl–AgCl (2 wt.%) reference electrode was used. At the final stage of each set of experiments this reference electrode was immersed in the melt for a short time for determination of the potential peaks, the melt being no longer used after this immersion.

The electrolytic processes with accumulation of electrodeposited products were performed in galvanostatic mode. The cell, as a platinum crucible (30 mm diameter, 40 mm high), was placed inside a cylinder vessel made of heat-resistant steel with a brass water cooled lid. The vessel was filled with pure argon. Heating of the electrolyser was carried out in a shaft furnace with silicon carbide heaters; the temperature was maintained with the accuracy of $\pm 2^\circ C$. The anode (a tantalum square plate 3 mm thick) was placed at the bottom of the platinum crucible. Molybdenum rods (5 mm in diameter) were used as cathodes. Each portion of an electrolyte (about of 40 g) served for a single cathodic deposition cycle only. To accumulate the product in each cycle a 5400 coulombs of electricity was passed. Cathodic products, after cooling to room temperature in argon atmosphere, were washed from the entrapped salt phase with 10%-hydrochloric acid, then washed with distilled water and ethanol and finally dried in air at $40^\circ C$.

A X-ray powder diffractometer DRON 2 supplied with computer data processing was used for the identification of the cathode products and electrolyte phase composition. A Stoe IPDS II diffractometer (Mo $K\alpha$ radiation) and the program JANA 2000 were used for the collection of experimental X-ray diffraction data and refinement of single crystal structure, respectively.

3. Results and discussion

Electrolytic processes with accumulation of cathodic products were for the most part carried out in electrolytes containing from 1.25 to 10 wt.% K_3TaOF_6 dissolved in the CsCl melt. According to the XRD study, quenched electrolyte samples did not contain any other (new) phase in addition to the initial CsCl and K_3TaOF_6 in predetermined proportions. A few experiments were conducted using Cs_3TaOF_6 as a Ta-containing electrolyte component. The XRD results indicated that in this case the $xCs_3TaOF_6-yCsCl$ compound is formed after melting of the CsCl– Cs_3TaOF_6 mixture.

3.1. Phase composition of electrolysis products

The change in phase composition of cathodic products obtained by electrolysis in the CsCl– K_3TaOF_6 molten system as

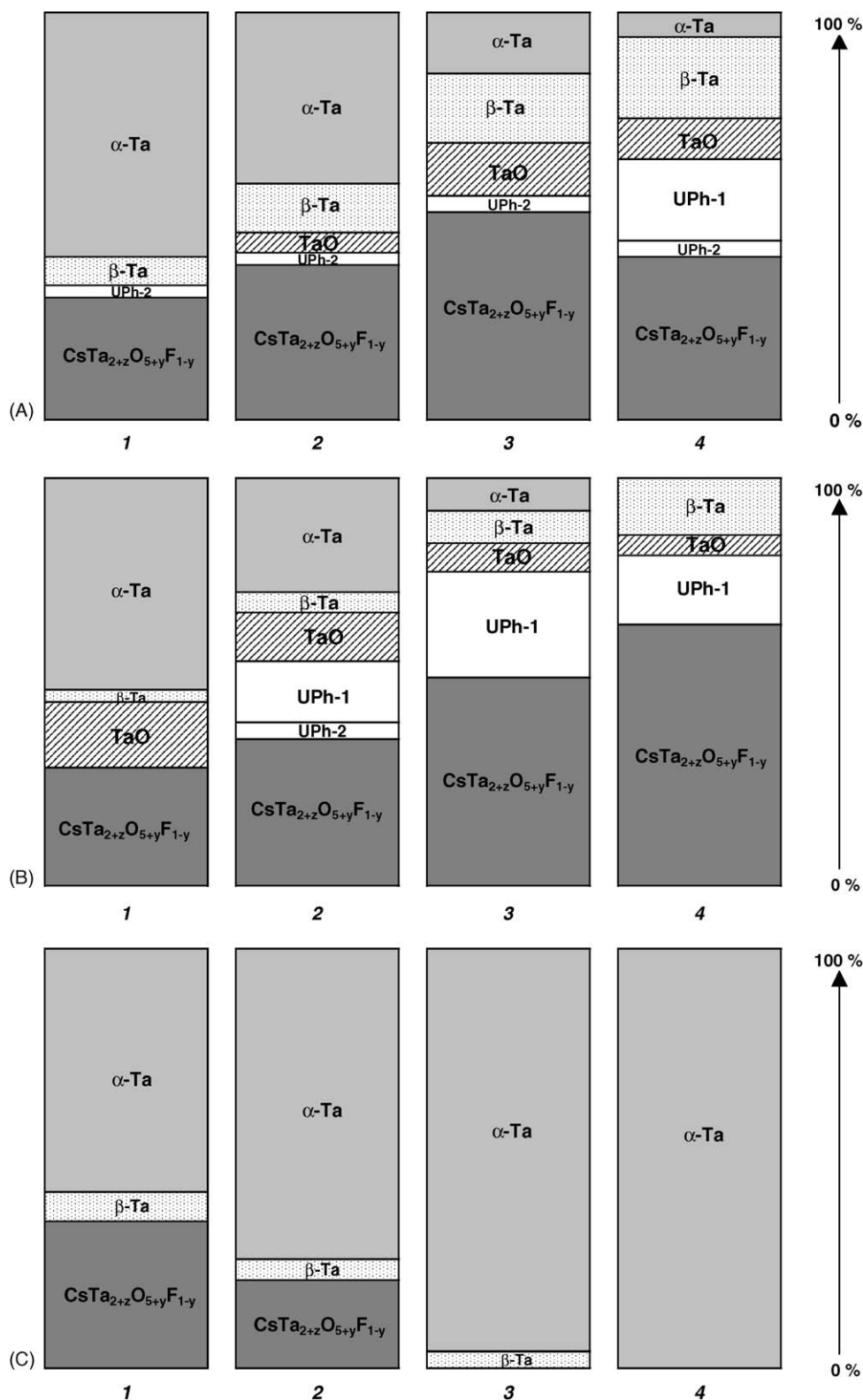


Fig. 1. Diagrams of the phase composition evolution of the cathodic products deposited at 0.15 A cm^{-2} with increasing of K_3TaOF_6 concentration in the CsCl melt: 1.25 wt.% (1), 2.5 wt.% (2), 5.0 wt.% (3) and 10 wt.% (4) for temperatures: 650 °C (A), 750 °C (B) and 850 °C (C).

a function of K_3TaOF_6 concentration is shown in Fig. 1A–C at temperatures 650, 750 and 850 °C, respectively. Fig. 2 indicates how the phase composition depends on cathodic current density for a 2.5 wt.% K_3TaOF_6 melt at 750 °C.

As can be seen from Figs. 1 and 2, several phases generally crystallized at the cathode simultaneously. The set of phases in cathodic deposits depends on all electrolysis parameters and may include the following phases:

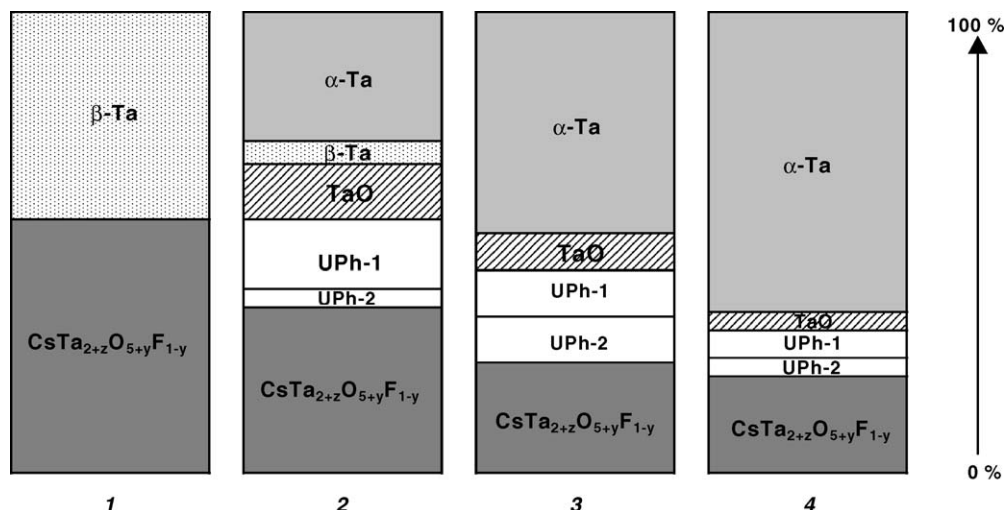


Fig. 2. Diagrams of the phase composition evolution of the cathodic products deposited at 750 °C in the CsCl–2.5 wt.% K_3TaOF_6 melt with increasing of the cathodic current density: 0.05 $A\ cm^{-2}$ (1), 0.15 $A\ cm^{-2}$ (2), 0.25 $A\ cm^{-2}$ (3) and 0.5 $A\ cm^{-2}$ (4).

- α -Ta – the cubic tantalum modification with body-centered crystal lattice [9], which is a unique tantalum modification produced by universally accepted metallurgical techniques.
- β -Ta – the tetragonal tantalum modification whose structure belongs to the Frank–Kasper structures of σ -type [10], which are typical for binary intermetallic compounds such as Fe–Cr. Tantalum of this modification could be apparently prepared only in the presence on an electric field: by direct current magnetron sputtering [11] or using the electrodeposition from molten salts [12,13]. The structure of β -Ta was described in detail in our publication [14]:
- TaO – the lower tantalum oxide with tetragonal crystal lattice [15].

Two different types of octahedral crystals with the similar general composition $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$. Here the oxidation state of Ta (n^+) depends on both a number of intercalated tantalum ions (z) and a number of fluorine ions replaced by oxygen ions (y) in the structure through the electroreducing process. From the charge balance, $n = (10 + y)/(2 + z) \leq 5$; hence $y \leq 5z$. These crystals have been deposited at the cathode during most of electrolysis cycles. The lamellar crystals of the first type (I) are transparent, colorless and dielectric similar to the ones described in [16]. The crystals of another type (II) are black and metal-like, pointing to an oxidation state of the Ta ion lower than 5. The relative amount of the crystals I in reference to the crystals II in the cathodic deposits was not more than 1/10. Peculiarities of the compounds I and II structures will be discussed below in special paragraph:

- UPh-1 – a conductive phase, which is present always only together with the phase- $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$, and as the latter has a metallic appearance. Its chemical composition is not yet determined because of difficulties to isolate it from other metal-like phases presenting in deposits.
- UPh-2 – beige colored scales of various tinge, which also were always deposited together with the phases I and II. According

to XRD data, the phase UPh-2 is a full structural analogue of the hexagonal calcite $CaCO_3$. Its chemical composition is under study.

SEM images of some characteristic phases obtained by electrolysis in CsCl– K_3TaOF_6 melt are shown in Fig. 3. X-ray patterns of one of the most multiphase deposits, and two individual phases: $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ and UPh-2 are displayed in Fig. 4.

As can be seen from the diagrams of Fig. 1, compounds $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ abound in all electrolysis products obtained at temperatures 650 and 750 °C without regard to parameters of the electrolytic process. At these temperatures the total relative share of all nonmetallic phases has tendency to increase as the K_3TaOF_6 concentration increases in the melt with the most significant growth of $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ phase amount. As regards to the composition of metallic fraction (α -Ta + β -Ta) the proportion of β -Ta phase monotonically increases in it with increasing of the K_3TaOF_6 concentration.

An opposite regularity takes place at the highest of tested temperatures – 850 °C. In this case $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ phase was presented in cathodic deposits only when the K_3TaOF_6 concentration did not exceed 5 wt.%, and no other nonmetallic phases formed in cathodic products at any K_3TaOF_6 concentrations. As to metallic tantalum, it mainly crystallized in the cubic modification. In any event, the metastable phase of β -Ta, even deposited at the cathode, should quickly transform to the thermodynamically stable α -Ta phase at such high temperature [13].

Fig. 2 shows that cathodic current density has the certain effect on the relationship between amounts of metallic and nonmetallic phases in electrolysis products obtained at the temperature 750 °C and concentration 2.5 wt.% K_3TaOF_6 in the melt. At the same time the β -Ta phase may be only deposited at relatively low current densities, no more than 0.15 $A\ cm^{-2}$ giving way to another tantalum modification and the proportion

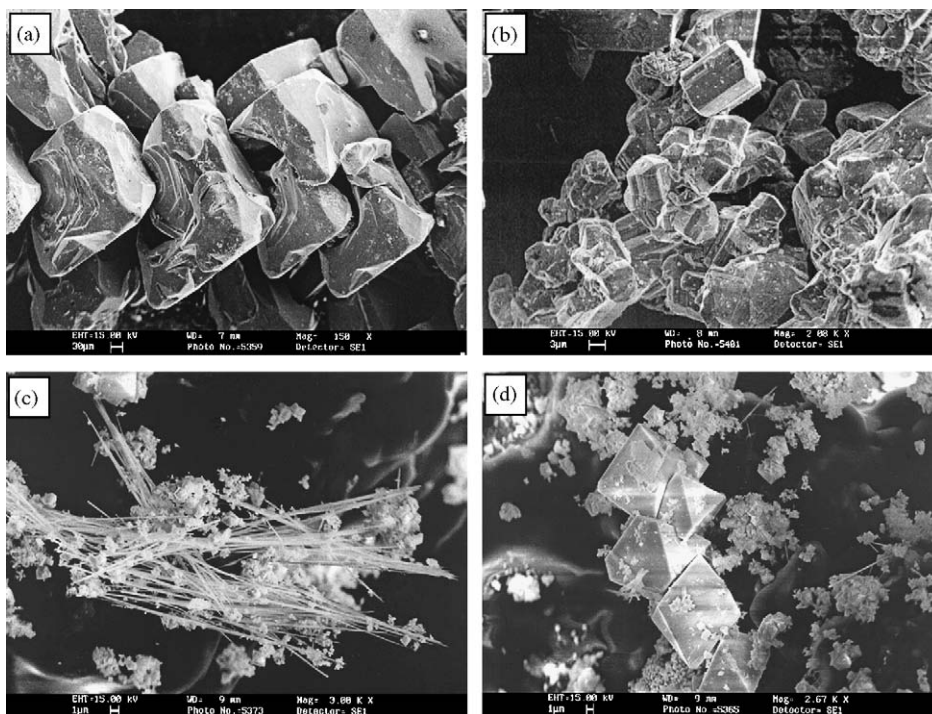


Fig. 3. SEM images of some characteristic phases obtained by electrolysis in the CsCl–K₃TaOF₆ melt: (a) α-Ta electrolytic crystal extracted from the cathodic product obtained at 750 °C and 0.15 A cm⁻² in the CsCl–1.25 wt.% K₃TaOF₆ melt, (b) typical crystalline aggregations of the β-Ta phase in the deposit obtained at 750 °C and 0.15 A cm⁻² in the CsCl–2.5 wt.% K₃TaOF₆ melt, (c) and (d) different segments of the cathodic product obtained at 650 °C and 0.15 A cm⁻² in the CsCl–5 wt.% K₃TaOF₆ melt. Thin needles of TaO (c) and octahedral crystals of the CsTa_{2+z}ⁿ⁺O_{5+y}F_{1-y} phase (d) present the main part of the product.

of CsTa_{2+z}ⁿ⁺O_{5+y}F_{1-y} phase decreases as the current density increases.

From the data presented in Figs. 1 and 2 it may be concluded that high temperature and low current density will conduce to reducing of phase number in cathodic deposits, since electrochemical process conditions in these cases should be most close to equilibrium.

Unfortunately now we are not able to explain in more detail the changes of phase composition as a function of parameters (Figs. 1 and 2). For strict correlation of cathodic product composition and electrodeposition parameters, the results of potentiostatic electrolysis will be provided, which is the task of current studies.

The above results were obtained when Ta-ions were introduced in an electrolyte with K₃TaOF₆. Therefore, potassium cations as well as caesium ones could be present in the second coordination sphere of tantalum complexes in the melt. In this

connection it was interesting to estimate the phase composition of cathodic products obtained when only caesium species are presents in molten electrolyte.

Table 1 shows that replacing of K₃TaOF₆ by Cs₃TaOF₆ has not a very great effect on the composition of cathodic products. The result obtained was rather unexpected, considering that such a substitution led to a considerable change in electrolyte phase composition as was noted above.

3.2. Structural investigation of CsTa_{2+z}ⁿ⁺O_{5+y}F_{1-y} (n ≤ 5) phases

Only CsTa₂ⁿ⁺O₅F has been described before with the highest oxidation state of Ta [16]. The published structural data only give the cationic positions. Our single crystal investigations of (I) and (II) confirmed the main cationic positions of Cs and Ta ions obtained by Babel et al. [16] and indicated clearly that both types

Table 1

Phase compositions of cathodic products obtained at temperature 750 °C and $d_c = 0.15$ A cm⁻² in CsCl–K₃TaOF₆ and CsCl–Cs₃TaOF₆ melts

Ta-containing compound in the melt	Concentration of M ₃ TaOF ₆ ^a (M = K or Cs)	Phase composition of cathodic products (wt.%)					
		α-Ta	β-Ta	CsTa _{2+z} O _{5+y} F _{1-y}	TaO	UPh-1	UPh-2
K ₃ TaOF ₆	2.5	28	5	36	12	15	4
Idem	10.0	0	14	64	5	17	0
Cs ₃ TaOF ₆	4.1	35	7	42	14	0	2
Idem	16.6	2	9	73	2	14	0

^a The concentrations of K₃TaOF₆ and Cs₃TaOF₆ (wt.%) are equivalent regarding the amounts of Ta⁵⁺ in a melt.

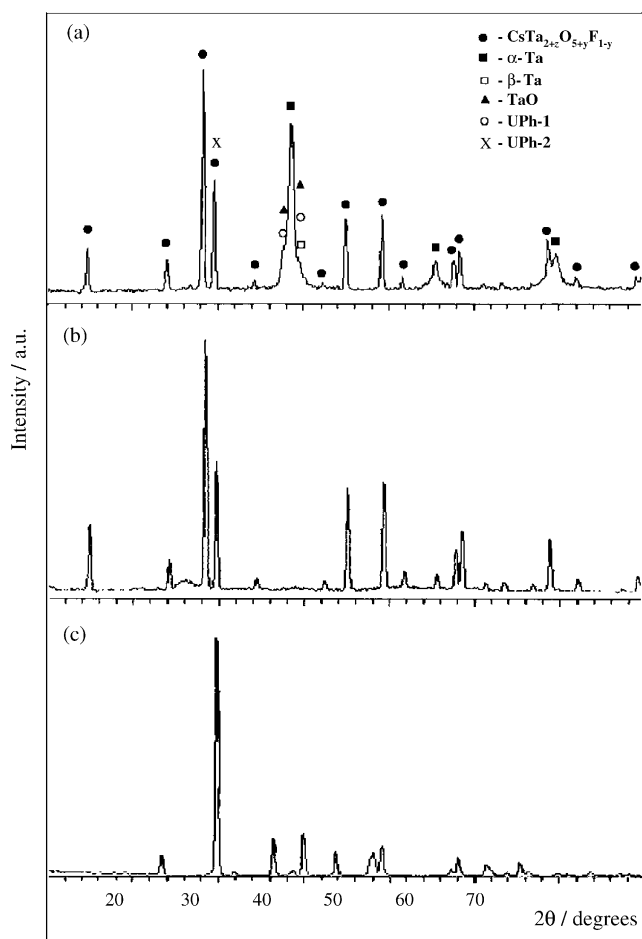


Fig. 4. XRD patterns of the deposit presented at diagram B2 of Fig. 1 (a) and of two separated individual phases: $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ (b) and UPh-2 (c).

of crystals are isostructural to $\text{RbTa}_2\text{O}_5\text{F}$ [17] with the same space group $Fd\bar{3}m$, the same unit cell parameter, $a = 10.499(1)$ Å, and the same positions of the basic ions (Table 2). Both structures were refined with high accuracy (R -factors equal to 0.0223 and 0.0172 for type I and II crystals, respectively).

The main building element of the structure type (Fig. 5) can be described as a pyrochlor framework with the chemical composition TaX_3 . The framework consists of $[\text{TaX}_6]$ -octahedrons shar-

Table 2
Structural characteristics of $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ ($n \leq 5$)

Atom	Wyckoff position	Coordinates in the unit cell ($x y z$)	Population coefficient, p
Ta	16c	(000)	1
Cs	8b	(1/8 1/8 5/8)	1
$X = (\text{O}, \text{F})^a$	48f	(7/8 y 7/8); I: $y = 0.0626(5)$; II: $y = 0.0630(3)$	1
Ta_{int}	8a	(7/8 7/8 7/8)	I: 0.018(4); II: 0.006(1)

The variable parameters are given for two different crystals: I (transparent and colorless); II (black-metallic).

^a Both O^{2-} and F^- anions occupy statistically the common structural position $X = (\text{O}, \text{F})$.

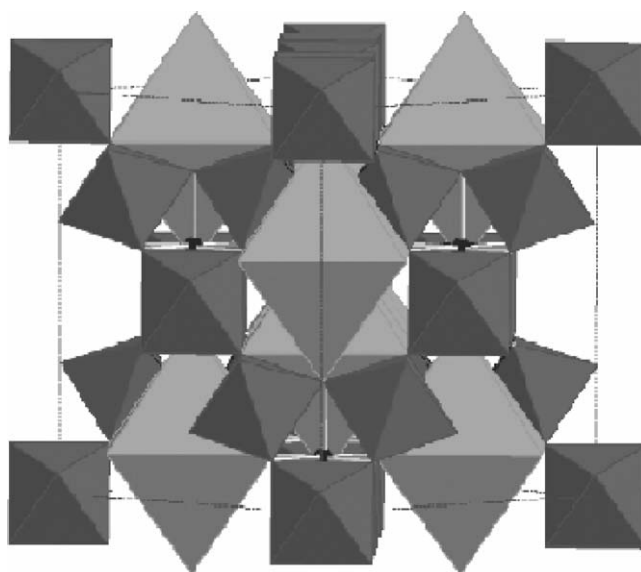


Fig. 5. Crystal structure of $\text{CsTa}_{2+z}{}^{n+}\text{X}_6$ ($n < 5$), where anion $X = (\text{O}, \text{F})$. The pyrochlor-like framework consists of $[\text{TaX}_6]$ -octahedra (dark gray color) sharing all their vertices. The Cs atoms are located in large light gray color of the framework. Positions of intercalated Ta atoms are shown by the black small circles connected with nearest anions (vertices of polyhedron). The cubic unit cell is indicated with dotted lines.

ing all their vertices. The chemical composition of the framework and the connection between octahedrons are analogous to Ta-bronzes [18]. The Cs ions are located in large octahedron formed by the anions (Cs–X distance is equal to 3.276(6) and 3.279(5) Å in I and II, respectively). Both types of crystals are characterized by intercalations defects: the $8a$ position is slightly occupied with Ta_{int} ions (Table 2). These additional atoms are located in the center of $[\text{Ta}_{\text{int}}\text{X}_6]$ -octahedron, similar to the $[\text{TaX}_6]$ -octahedron of the framework. The difference between crystals I and II is revealed in the concentration of the defects: the number of defects per unit cell in I is three times larger than in II (the p coefficient in Table 2).

The $\text{Ta}_{\text{int}}\text{--O}$ and Ta--O distances are equal to each other for I (1.970(5) and 1.969(2) Å, respectively), while for II, the $\text{Ta}_{\text{int}}\text{--O}$ distance is larger than the Ta--O distance (1.974(5) and 1.970(2) Å, respectively). This difference indicates that the Ta_{int} ions have the oxidation state $n = 5$ in I and $n < 5^+$ in II. The increase of the $\text{Ta}_{\text{int}}\text{--O}$ distance is associated with increasing Ta_{inc} ionic radius in II, due to reduction of their oxidation state. The overall electroneutrality is most likely controlled by the amount of F-ions in the mixed anion position X. The F/O ratio is larger in II than in I, owing to the higher defect concentration and higher oxidation state of all Ta ions in I. Taking into account the structural data and the oxidation state of the Ta ions in I which is equal 5, the formula of I can be more precisely expressed as $\text{CsTa}_{2.01}{}^{5+}\text{O}_{5.05}\text{F}_{0.95}$. The partial reduction of Ta ions does not allow to give a single-valued formula for crystal II. In contrast to the compounds under discussion, it is interesting to mention that the anionic composition of the $[\text{TaX}_3]$ framework, that is F/O ratio, is constant regardless of the tantalum oxidation state in Ta-bronzes [18,19].

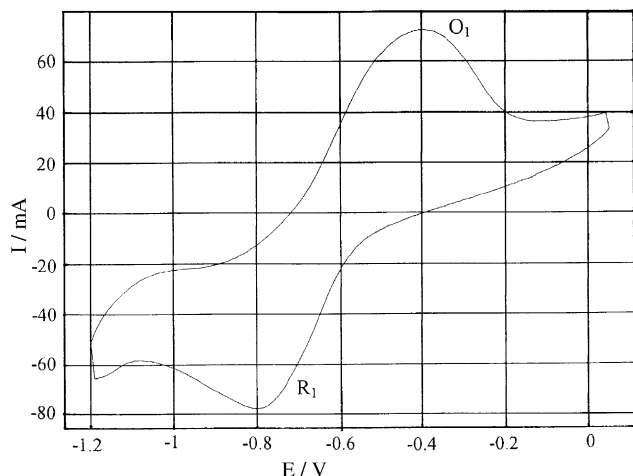
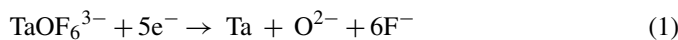


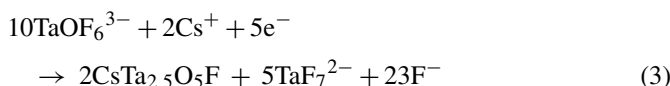
Fig. 6. Cyclic voltammograms at silver electrode in CsCl–K₃TaOF₆ melt. Area: 0.447 cm². Sweep rate: 0.2 V s⁻¹. Temperature: 700 °C. Concentration of K₃TaOF₆: 1.01 × 10⁻⁴ mol cm⁻³. Quasi-reference electrode: glassy carbon.

3.3. Study of electrochemical reduction of tantalum oxyfluoride complexes in CsCl

Polarization curves for tantalum oxyfluoride complexes in CsCl melt were obtained by cyclic voltammetry method. Fig. 6 shows that a discharge peak (*R*₁) and a newly developing peak at around -1.1 V in the potentials region up to -1.2 V at 700 °C (relative to the GC quasi-reference electrode) are observed on cyclic voltammograms in CsCl–K₃TaOF₆ melt. The nature of the latter peak will be discussed below. According to [20], this peak corresponds to the discharge of tantalum monoxyfluoride complexes to tantalum metal or its monoxide TaO, evidently by the reactions



In the presence of Cs⁺ outer-sphere cations in the melt, the discharge of TaOF₆³⁻ anions with the formation of low-valence pyrochlor type phase also seems to be occurring at the peak *R*₁ potential. A plausible reaction for the case of Ta(V) to Ta(IV) electrochemical reduction should be as follows:



Rather large width of the peak *R*₁ on the curve recorded at 700 °C (Fig. 6) is probably just a consequence of simultaneous passage of all above-listed reactions at close potentials.

The effects of K₃TaOF₆ concentration in the melt and polarization scan rate (*v*) on the peak current (*I*_p^c) and the peak potential (*E*_p^c) of the TaOF₆³⁻ complexes electroreduction were studied at temperature 700 °C. The following peculiarities were established: *E*_p^c shifted to the negative direction with increasing of *v*, but the potential shift is not very significant up to 0.3 V s⁻¹. The *I*_p^c/*v*^{1/2} ratio decreases as *v* increases up to 0.3 V s⁻¹. *E*_p^c is essentially independent of K₃TaOF₆ in the concentration range from 4 × 10⁻⁵ up to 3.5 × 10⁻⁴ mol cm⁻³. Taking into account

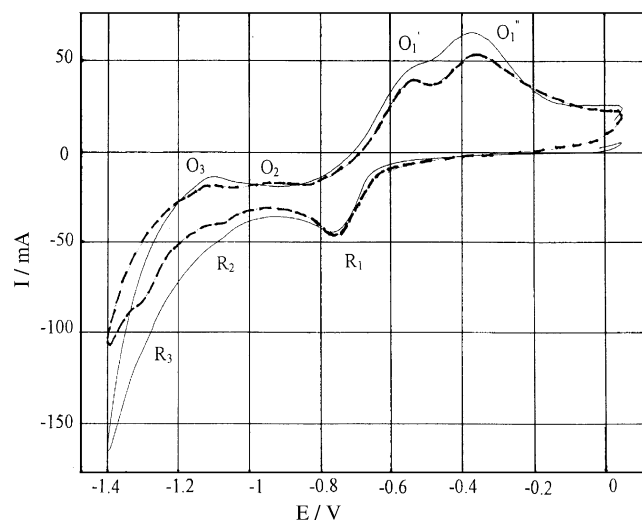
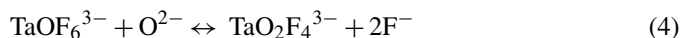


Fig. 7. Cyclic voltammograms at silver electrode in CsCl–K₃TaOF₆–K₃TaO₂F₄ melt. Area: 0.353 cm². Sweep rate: 0.1 V s⁻¹. Temperature: 810 °C. Concentration of K₃TaOF₆: 9.62 × 10⁻⁵ mol cm⁻³. Concentration of K₃TaO₂F₄: 8.41 × 10⁻⁵ mol cm⁻³. Quasi-reference electrode: glassy carbon. Dashed line: before addition of K₃TaO₂F₄. Solid line: after addition of K₃TaO₂F₄.

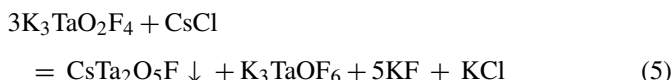
these peculiarities, it may be concluded that most likely the electroreduction process proceeds quasi-reversibly with a preceding chemical reaction. Probably, such a chemical reaction is a partial dissociation of the TaOF₆³⁻ complexes in the diffusion layer, which is associated with the differences in bonds lengths between tantalum as central atom and various ligands. Analytical solution of such a kind of process is unknown, so no calculation of the number electrons and others kinetic parameters is available.

Fig. 7 shows cyclic voltammograms of the CsCl–K₃TaOF₆ melt at temperature 810 °C obtained at more extended potentials range. Three cathodic waves (*R*₁, *R*₂ and *R*₃) are detected on these voltammograms and three corresponding peaks of electrooxidation. Presence of *R*₂ wave in a melt containing initially only monoxyfluoride complexes can be explained by the generation of free oxygen anions in the near-electrode layer due to the cathodic process (1) and by occurrence of the exchange reaction



The tantalum dioxyfluoride complexes that are formed by reaction (4) are discharge at more negative potential than monoxyfluoride ones (Fig. 7). To confirm our supposition regarding the nature of *R*₂ wave, 1.0 g of K₃TaO₂F₄ synthesized beforehand was added to the melt containing 60 g of CsCl and 3.3 g of K₃TaOF₆. Some increase of *R*₂ wave height was observed after addition (Fig. 7). The wave *R*₂ after addition of K₃TaO₂F₄ had not clear peak, but there was a bend observed on the voltammogram in the region of potentials corresponding to wave *R*₂. This fact corroborates that *R*₂ is just the wave related to the discharge of the TaO₂F₄³⁻ complexes. But increase of *R*₂ wave height was not proportional to the quantity of added K₃TaO₂F₄. That can be explained by the fairly low solubility of K₃TaO₂F₄ in the CsCl melt. Indeed, about 0.4 g of a bottom

deposit was observed in the reaction vessel after the experiment. According to chemical analysis and XRD data, this deposit represented the monophase of the $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ compound, which can be formed possibly by reaction of CsCl with the rest of $\text{K}_3\text{TaO}_2\text{F}_4$ undissolved in the melt



Rather low solubility of $\text{K}_3\text{TaO}_2\text{F}_4$ in molten CsCl is also manifested in moderate distinction in phase composition of cathodic deposits obtained in CsCl– K_3TaOF_6 melts with and without addition of potassium dioxyfluorotantalate. Thus, with addition of 1.5 wt.% of $\text{K}_3\text{TaO}_2\text{F}_4$ to the melt containing 2.5 wt.% of K_3TaOF_6 the proportion of Ta metal in the deposits produced at temperature 750 °C and $d_c = 0.05 \text{ A cm}^{-2}$ decreased from 45% (Fig. 2, diagram 1) to approximately 40% and the proportion of $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ increased, respectively from 55 to 60%.

As to peak R_3 around –1.3 V in Fig. 7, it can be attributed to the alkali metal cations discharge on the surface of deposited products at the potentials of R_1 and R_2 waves. A depolarization observed at the curves of Fig. 7 is most likely caused by a reduction reaction of these products by an alkali metal. This supposition correlates well with the results of our investigation of the effect of cathodic current density influence on the electrolysis products phase composition. Thus, exceeding a limiting diffusion current density of monooxyfluorotantalate complexes discharge (according to the steady-state voltammetry data it takes place at about 0.25 A cm^{-2} at 2.5 wt.% K_3TaOF_6 and temperature 750 °C) entailed an increase of the α -Ta phase proportion in cathodic deposits (Fig. 2). In this case, the cubic tantalum modification appears to be formed not only by direct electrochemical crystallization, but also by a metallothermic reduction of TaO or other tantalum compounds with potassium or caesium as reducing agents.

The diagrams of Figs. 1 and 2 favour the view that the electroreduction of TaOF_6^{3-} complexes can occur by reactions (1)–(3) at temperatures 650 and 750 °C. But at 850 °C the presence of TaO has not been observed in cathodic deposits. The latter suggests that in this case either cathodic process does not go by the reaction (2) or TaO formed by this reaction then decomposes into Ta and O_2 , since TaO is rather unstable composition and the Gibbs energy of its decomposition is very negative [20,21]. The kinetics of TaO the decomposition reaction is more rapid at the temperature 850 °C than for 750 °C.

This suggestion is in accordance with voltammetric curves obtained at temperature 700 and 850 °C (Fig. 8). Actually, at

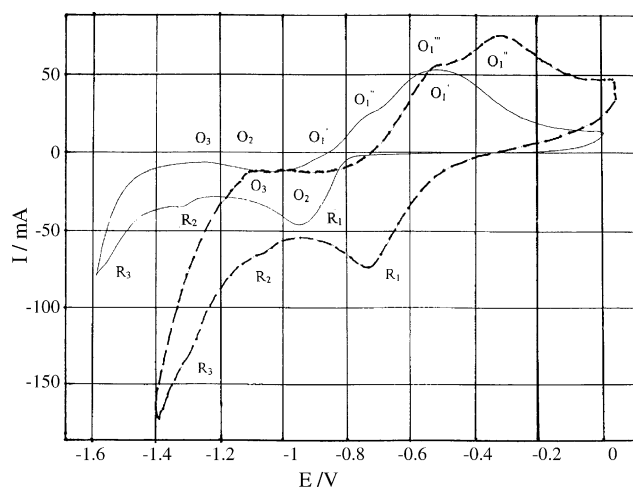


Fig. 8. Cyclic voltammograms at silver electrode in CsCl– K_3TaOF_6 melt. Area: 0.447 cm^2 . Sweep rate: 0.1 V s^{-1} . Concentration of K_3TaOF_6 : $1.01 \times 10^{-4} \text{ mol cm}^{-3}$. Reference electrode: Ag/NaCl–KCl–AgCl (2 wt.%). Solid line: temperature 700 °C. Dashed line: temperature 850 °C.

temperature 700 °C to wide peak R_1 corresponds three electrooxidation peaks (O'_1 , O''_1 , O'''_1) of products, which are formed during cathodic cycle (1)–(3). At the same time at temperature 850 °C to wave R_1 two corresponding electrooxidation peaks (O'_1 , O''_1) were observed in anodic one-half cycle (Fig. 8). These two waves were registered on the voltammograms at temperature 810 °C also (Fig. 7).

The electrochemical process (1), which is accompanied by the generation of free, not bonded in complexes oxygen anions in near-electrode layer may result in local chemical reactions in this layer with formation of dielectric Ta^{5+} -compounds, for example



Other possible reason for the nucleation of Ta^{5+} -compounds phases during electrolysis may be local fluctuations of the melt composition in near-cathode layer associated with selective removal of tantalum species from the melt by their cathodic discharge. When nucleated, a Ta^{5+} phase gains possibility to grow using Ta^{5-x} compound crystals formed by electroreduction reaction (3) as a seed. Low conductivity of these crystals, which is related to low concentration of intercalation defects in the $\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$ structure (Table 2) that makes possible such a performance.

Table 3
Phase compositions of cathodic products obtained at temperature 750 °C and $d_c = 0.15 \text{ A cm}^{-2}$ in melts with various proportions CsF in the solvents for K_3TaOF_6 (5 wt.%)

Mole fraction of CsF in a solvent for K_3TaOF_6	Phase composition of cathodic products (wt.%)					
	α -Ta	β -Ta	$\text{CsTa}_{2+z}\text{O}_{5+y}\text{F}_{1-y}$	TaO	UPh-1	UPh-2
0	8	8	51	7	26	0
0.5	22	58	12	0	0	8
1	16	84	0	0	0	0

Our tentative experiments using additions of caesium fluoride to the foregoing melts show (Table 3) that replacing of CsCl by CsF in solvents for K_3TaOF_6 leads to a considerable increase of metal phases proportion (especially β -Ta) in cathodic products with corresponding diminution of $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ and other nonmetallic phases. Such phenomena can be associated with increase of solubility and the strength of tantalum oxyfluoride complexes as the amount of F-ions increases in the melt [22].

4. Conclusions

The basic regularities of variations in phase composition of cathodic products obtained in CsCl– K_3TaOF_6 and CsCl– Cs_3TaOF_6 molten systems at different electrolysis parameters have been established. Multiphase deposits are crystallized as a rule, and the number of phases inherent in one deposit can be as more as six suggesting that electrocrystallization nonequilibrium conditions for the most instances. Cathodic products can be formed both by a direct electrochemical reduction and through chemical reactions accompanying electrolysis process.

Unknown so far in the literature the low-valency tantalum compound $CsTa_{2+z}^{5-x}O_{5+y}F_{1-y}$ with a pyrochlor-like crystal lattice is the most typical phase in electrolysis products in melts containing caesium cations. This compound was present in almost all obtained cathodic deposits. At the same time the conditions for electrodeposition only of pure, almost oxygen-free tantalum metal even from oxygen-containing melts were found.

The preparation by electrochemical way of $CsTa_{2+z}^{n+}O_{5+y}F_{1-y}$ ($n \leq 5$) compounds in a single crystal form made it possible to examine special features of their structures. A number of resemblances and distinctions in structures of transparent dielectric crystals ($n=5$) and metal-like conductive crystals ($n < 5$) have been revealed. It was found that the framework tantalum atoms are apparently not reduced during electrocrystallization, and the Ta_{int} ions are only subjected to the electrochemical reduction. At the same time the framework anion composition is modified as a consequence of reduction process: the F/O ratio in mixed position X = (O, F) is increased.

Earlier we have studied the phase composition of the cathodic products obtained by electrolysis in melts using lithium, sodium and potassium halides as solvents for K_3TaOF_6 and $K_3TaO_2F_4$ [8,18,19]. In contrast to the molten systems studied in the present work, tantalum oxide bronzes (hexagonal, tetragonal and cubic), but not compounds with pyrochlor type structure, have been crystallized in these melts besides tantalum metal and TaO. The cause of this fundamental distinction can be as follows. In certain electrolysis conditions crystallization of tantalates and fluorotantalates take place in both cases. The $[TaO_3]^-$ framework of these compounds has cavities or channels whose dimensions correspond to the sizes of alkali metal ions neutralizing a charge of the framework. The Cs^+ cation is too large to be settled in channels of bronze type frameworks, and a pyrochlor framework with octahedral cavities is more appropriate for it; the distances

M–X, where M is an alkali metal, and X = (O, F), are 3.05 Å for Cs–O and 2.0, 2.35 and 2.70 Å for Li–O, Na–O and K–O, respectively [23].

Preliminary results of CsF influence addition to CsCl– K_3TaOF_6 electrolytes on the phase composition of cathodic products have been obtained. The appreciable influence was found. This is a good reason for investigations in detail the processes in molten electrolytes with CsF as solvent for oxyfluorotantalate compounds. In contrast to chlorides, alkali metal fluorides dissolve well not only monooxyfluorides of tantalum (where O/Ta = 1), but also their dioxyfluorides (O/Ta = 2). That will permit to study chemical and phase compositions of cathodic products to be obtained at a higher oxygen content in melts.

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