

COMPOSITION OF OUTER-SPHERE CATIONS AS A TOOL FOR ELECTROCHEMICAL SYNTHESIS OF NOVEL NIOBIUM COMPOUNDS

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Abstract

The individual alkali-metal cation influence on the chemical and phase composition of electro-synthesis products has been studied in fluoride solvents with different O/Nb ratios. It was shown that the cation nature of molten electrolytes is a powerful tool to control the chemical and phase composition of the cathodic products of electrolysis in oxy-fluoride and fluoride melts. New niobium compounds were obtained by electrochemical synthesis using the outer-sphere cations composition control: tetragonal Nb_6O , rhombohedral sub-oxide Nb_xO ($x < 6$) and composite compounds " NbO "- n " MeF " ($Me=K, Rb, n=1, 2$).

Keywords: Niobium-oxide compounds, molten salts, outer-sphere cation, electrochemical synthesis

1. Introduction

Electrolysis in molten salts has an advantage over other known methods of plating (plasma spraying, chemical condensation from vapor phase and so forth). It permits producing pure, plastic, nonporous and coherent layers of refractory metals on extensive substrates of complex configuration. Another field of electroplating application is the complex shaped articles manufacturing by galvanoplastics. At last, molten salts electrolysis is an effective method to produce expensive niobium and its alloys (with

tungsten, molybdenum and zirconium) by recycling their substandard wastes. This technology is successfully used in the Russian industry.

As the main component of the electrolyte for niobium electrolysis a complex fluoride $Nb(V)-K_2NbF_7$ is commonly used together with alkali metal chlorides and/or fluorides as solvents [1]. However, the real ionic composition of a salt system is formed only after the salt fusion as the result of reduction-oxidation processes of complex formation in the melt.

One of the most important factors affecting the working electrolyte composition is oxygen concentration. In industrial practice, the melts for niobium electrolysis contain oxygen impurities in a wide range of concentrations. The presence of this impurity in the melt can be hardly prevented without great expenses and forces. A lot of ways for oxygen to enter the bath exist – it is introduced with various initial components (electrolyte constituents, anode material) or from the atmosphere of electrolyzer. Nevertheless, as it will be demonstrated below, the presence of oxygen in the bath does not necessarily lead to the considerable contamination of cathodic product. The deposit purity depends on the electrolysis conditions, which could be appropriately chosen.

In recent years the behavior of oxygen, namely of oxygen-containing niobium species, in electrochemical processes has drawn the attention of researchers [2-11]. The reason is apparent: oxygen is one of the most harmful impurities in niobium, affecting drastically the mechanical and electrophysical properties of this refractory metal. The problem of oxygen in refractory metal compounds electrolysis has got one more aspect over the past decade. It is related to the possibility of novel compounds electrosynthesis in the $Nb-O$, $Nb-O-F$, $Nb-O-F-Me$ systems (Me is an alkali metal) [12, 13]. These new compounds are interesting from practical point of view due to their unusual structures and unusual valence states of the refractory metal.

The nature of anion in a solvent has a significant effect on the electrochemical behavior of both niobium and oxygen: the mechanisms of niobium complexes cathodic reduction differ in molten fluorides and chlorides and corresponding cathodic products have different chemical and phase composition [1]. At the same time, the solvent cationic composition role in electrochemical processes remained out of focus. This has an effect on a limited and non-functional choice of solvents employed in practice. They are, as a rule, the equimolar $NaCl-KCl$ mixture (occasionally with $CsCl$ additions) or the ternary $LiF-NaF-KF$ eutectic (FLINAK). The most attractive feature of both mixtures is evidently their rather low melting point (the minimum liquidus points are 658 and 453 °C, respectively). However, such a simplified approach to the choice of a solvent restricts the amount of information that could be obtained in electrochemical studies. Indeed, we may assume *a priori* that the outer-sphere surroundings of complex niobium anions composed of solvent cations should influence the structure and stability of these complexes as well as their electrochemical behavior. There are at least three possible mechanisms of the outer-sphere cations influence on complexes in molten salts [14]: competition between the cations for the ligand, the central atom-ligand bond polarization, and association of outer-sphere ions with complex ions to form ion couples.

In this paper, the character of the solvent individual cations influence is analyzed. It determines the second coordination sphere composition, the electrochemical reduction of niobium fluoride and oxy-fluoride complexes in melts with different O/Nb ratios and particularly, the chemical and phase composition of the cathodic products of electrolysis.

2. Experimental

Individual alkali-metal fluorides were commonly used as solvents. The exceptions were lithium and sodium fluorides. Their eutectic mixture was taken (61.3 mol. % LiF). Our preliminary studies showed that substitution of one of these salts by the other in this salt system did not modify its electrochemical behavior. At the same time, high melting point of these salts would displace the experimental temperature range toward high temperatures untypical for niobium electrochemistry.

Alkali metal fluorides (“chemical pure”) were purified by double melt re-crystallization. The fluoride was introduced into a glassy carbon crucible (SU-2000) and dried at 400-500 °C under vacuum, then heated to 50 °C above the melting point under argon, and slowly (3-4 °C h⁻¹) cooled down to 50 °C below the melting point. The solidified salt was then transferred at 120 °C to a dry-box and impurities were removed mechanically.

To produce K_2NbF_7 , the high-purity Nb_2O_5 was dissolved in a chemically pure hydrofluoric acid solution (50 wt %). Precipitation of K_2NbF_7 occurred on adding a saturated solution of potassium chloride at 80 °C. The product was filtered, washed with rectified ethanol and dried under vacuum at 70 °C. K_2NbOF_5 synthesis was performed melting K_2NbF_7 , Nb_2O_5 , and KF in appropriate ratios in a glassy carbon vessel under argon atmosphere.

Voltametric studies were conducted in a three-electrode cell under the atmosphere of carefully purified argon. The glassy carbon ampoule served as container for the melt and at the same time as the auxiliary electrode. Glassy carbon and platinum rods (1-2 mm) were used as working electrodes and glassy carbon plate - as a quasi-reference electrode.

The electrolytic processes with accumulation of electrodeposited products were performed in an electrolyzer - a molybdenum crucible (40 mm diameter, 50 mm high) placed inside a vessel made of heat resistance steel with a brass water cooled lid. Anode material (niobium monoxide) was placed on the bottom of the crucible. Molybdenum rods (5 mm diameter) were used as cathodes. Heating of the electrolyzer was carried out in a shaft furnace with silicon carbide heaters.

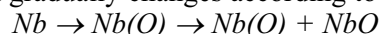
The testing procedure of molten salt systems (a niobium complex and a solvent) involved several cycles of galvanostatic electrolysis with a soluble anode (niobium monoxide) under the same controlled parameters ($t=750$ °C, $D_c=0.2$ A cm⁻², $Q=1.5$ A h/cycle). Due to the electrochemical dissolution of the anode and disbalance between the amounts of oxygen supplied into the electrolyte by the anode and released at the cathode,

the oxygen content of the melt was progressively increasing from cycle to cycle. So, each new cycle was performed in a kind of new electrolyte with relatively higher oxygen content than at the previous stage (electrochemical monitoring).

X-ray powder diffraction analysis, single crystal X-ray technique, scanning electron micrography, chemical and spectrum analysis and optical crystallography were also used.

3. Results and discussion

The first series of experiments was carried out in niobium and potassium fluoroniobate containing electrolytes (O/Nb molar ratio could change within $0 < Nb/O < 1$ from cycle to cycle). Our findings supported the assumption that the nature of the solvent cation correlated with the character of the cathodic process in oxyfluoroniobate complexes containing melts. The electrolytes with the $LiF-NaF$ solvent sharply differ from those with KF , RbF or CsF solvent in the amount of oxygen transferred from the electrolyte to the cathode. In the case of $LiF-NaF$ melt, the oxygen content of the cathodic deposits increases from cycle to cycle to attain about 10 wt % in the final cycle and their phase composition gradually changes according to the scheme:



The cathodic products of electrolysis with all remaining solvents were, up to final cycles, niobium metal with low oxygen content: hundredths (in KF , RbF) and tenths (in CsF) of percent; no clear correlation between this content and O/Nb ratio in the melt was traced.

The reason of the difference is evident from examination of the corresponding cyclic voltamograms (Fig. 1) in $LiF-NaF$ solvent and in molten salts containing larger cations. As can be seen, the mutual arrangement of the waves corresponding to the reduction of tetravalent niobium fluoride and oxy-fluoride complexes (the latter are formed in the melt through the initial Nb^{5+} ions reaction with niobium metal) is different in $LiF-NaF$ and KF . In $LiF-NaF$ (Fig. 1a), the oxy-fluoride (oxygen containing) complexes discharge (peak R_1) precedes that of the fluoride (oxygen-free) complexes (peak R_2); that explains the more intensive transition of oxygen into the cathodic products in the course of electrolysis in this system. In KF (Fig. 1b), the reduction potentials are inverted and oxyfluoroniobate complexes discharge at more negative potentials than fluoride complexes. Further increase in the radius of the solvent cation did not lead to principal changes of voltamograms.

To study the electrochemical behavior of the dissolved oxygen at its higher relative content ($1 < O/Nb < 2$), molten salt systems with starting ratio $O/Nb=1$ were subjected to electrolysis. Potassium mono-oxyfluoroniobate K_2NbOF_5 rather than fluoroniobate was used as niobium-containing component. Therefore, the initial electrolyte did not contain oxygen-free niobium complexes and the fraction of dioxyfluoride complexes was increasing from cycle to cycle at the expense of the mono-oxyfluoroniobate complexes.

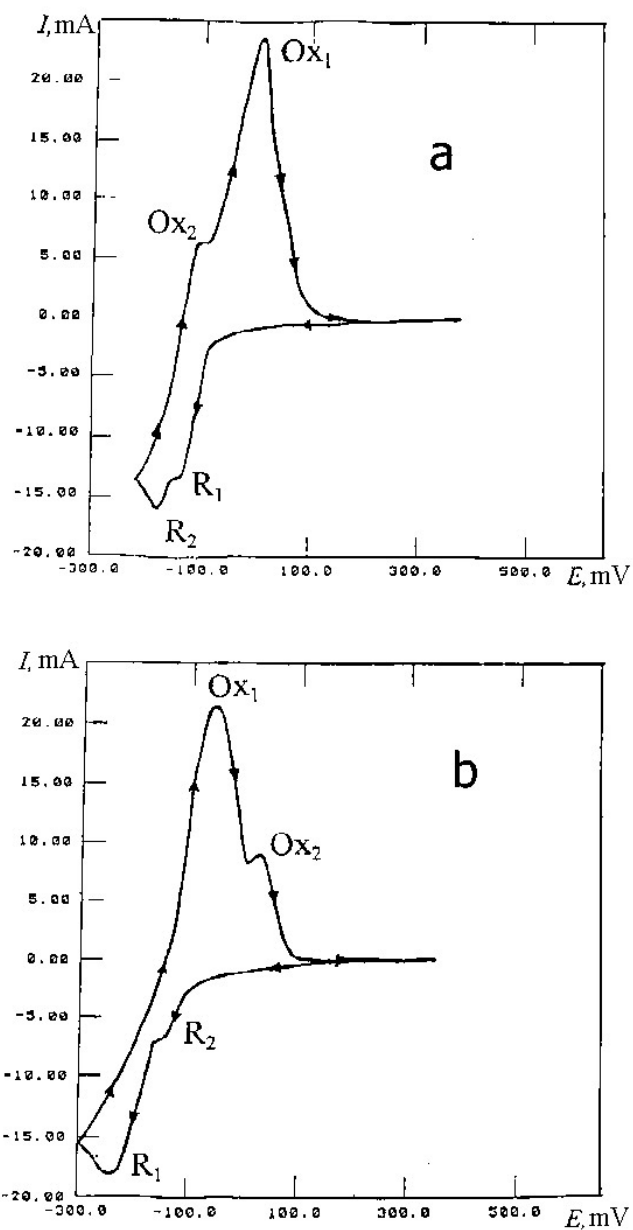


Figure 1. Cyclic voltammograms of (a) LiF-NaF and (b) KF melts containing 0.4 mol % K_2NbOF_5 and 0.08 mol % K_2NbF_7-Nb ; $t=850\text{ }^\circ\text{C}$, $v=0.2\text{ V s}^{-1}$, $A=0.14\text{ cm}^2$. Glassy carbon working, auxiliary and quasi-reference electrodes.

Fig.2 shows the progress in the cathodic product composition of successive cycles of electrolysis in the K_2NbOF_5 melts with different solvents. The height of the section symbolizing particular phase in the cathodic deposit is proportional to the content of this

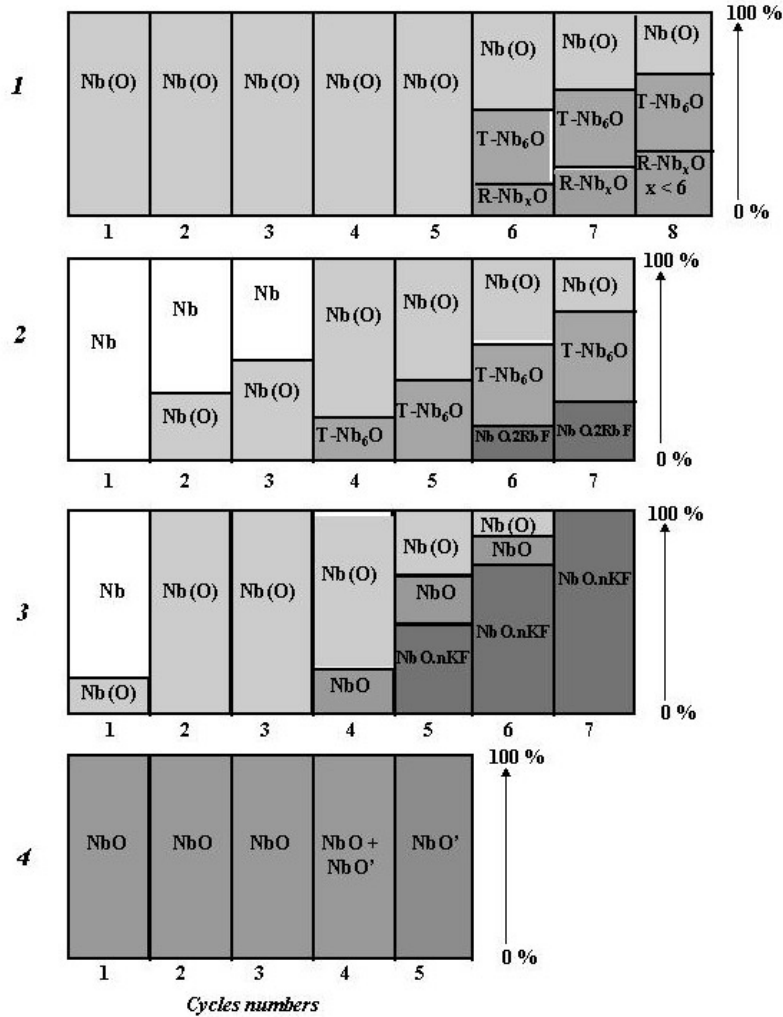


Figure 2. Phase composition (relative phase contents) of cathodic products obtained in successive cycles of galvanostatic electrolysis with a soluble NbO anode in the K_2NbOF_5 (0.05 mol) melts in (4) NaF-LiF, (3) KF, (2) RbF, and (1) CsF; $t=750\text{ }^\circ\text{C}$, $D_c=0.2\text{ A cm}^{-2}$, $Q=1.5\text{ A h/cycle}$, R and T designate rhombohedral and tetragonal structures, respectively.

phase in the deposit determined by quantitative X-ray powder diffraction patterns.

These diagrams once again demonstrate clearly that the phase composition of the electrolysis products in the system under study depends on the cationic composition of the solvent.

At certain cationic composition of the solvent a sufficiently pure (relative to oxygen) niobium can be obtained even from the melts with high oxygen content. For example, the use of *RbF* instead of *LiF-NaF* at $O/Nb=1$ results in a more than two-orders-of-magnitude decrease in the oxygen concentration of the cathodic product (other conditions being equal). However, this tendency, i.e. decrease in the amount of oxygen transferred from the melt to the cathodic product with increase in the solvent cation size, is valid only up to Rb^+ . The oxygen content of the cathodic deposits obtained by electrolysis in *CsF* melts is higher than that in the case of *RbF* electrolyte. The possible reason is a change in the coordination number of the oxyfluoride complex with respect to the alkali metal (Cs^+) whose size exceeds a definite limit (in our case Cs^+). This change is accompanied by decrease in the strength of complex.

At sufficiently high concentrations of dioxyfluoronioabate complexes in the melts, the cathodic products contain unknown or unidentified [12-13] oxygen-containing phases.

During electrolysis of the $K_2NbOF_5-LiF-NaF$ system, the deposition of the stoichiometric monoxide *NbO*, which occurs already in the first cycle of monitoring, is followed by the deposition of oxide phases with randomly distributed vacancies in *NaCl*-type structure, both in the oxygen and niobium positions (*NbO*). The oxygen content in these phases can be as high as $O/Nb=1.7$ [12].

Among the products of electrolysis of the K_2NbOF_5-CsF melt, the hitherto unknown sub-oxide Nb_xO ($x<6$) was identified; this oxide has a rhombohedral structure untypical of niobium compounds. The tetragonal sub-oxide Nb_6O was first obtained electrochemically by electrolysis of the above system or the K_2NbOF_5-RbF melt.

In our opinion, the most interesting feature of the electrolysis of K_2NbOF_5 in *KF* and *RbF* melts is the cathodic deposition of low-valence niobium composites “*NbO*”-*n*”*MeF*” ($Me=K, Rb, n=1, 2$). Here, “*NbO*” and “*MeF*” are layered fragments (atomic nets) of the cubic structures of *NbO* and *MeF*. The fragments alternate along a fourth order axis in the crystal lattices of these compounds. The general chemical formula of these composites is $Me_{2-x}Nb_4O_3(F,O)_3F$, and their crystal-chemical formula (determined by single crystal X-ray technique on a Syntex P1 automated diffractometer) is $[Nb_4O_3(O,F)_2] \cdot [MeF][Me, \square](Me, O)$, where \square -vacancy. The composite compound with $Me=K$ was first prepared by electrolysis of K_2NbOF_5 dissolved in FLINAK [13], and its rubidium analogue (Fig.3) was prepared for the first time in the present study.

Similar composite phases with $Me=Li, Na, \text{ or } Cs$ were not obtained. It can be explained by the fact that the unit cell parameter *a* of the “*MeF*” fragment is similar to the corresponding parameter of the “*NbO*” fragment ($a=4.21 \text{ \AA}$) only for $Me=K$ (4.12 \AA)

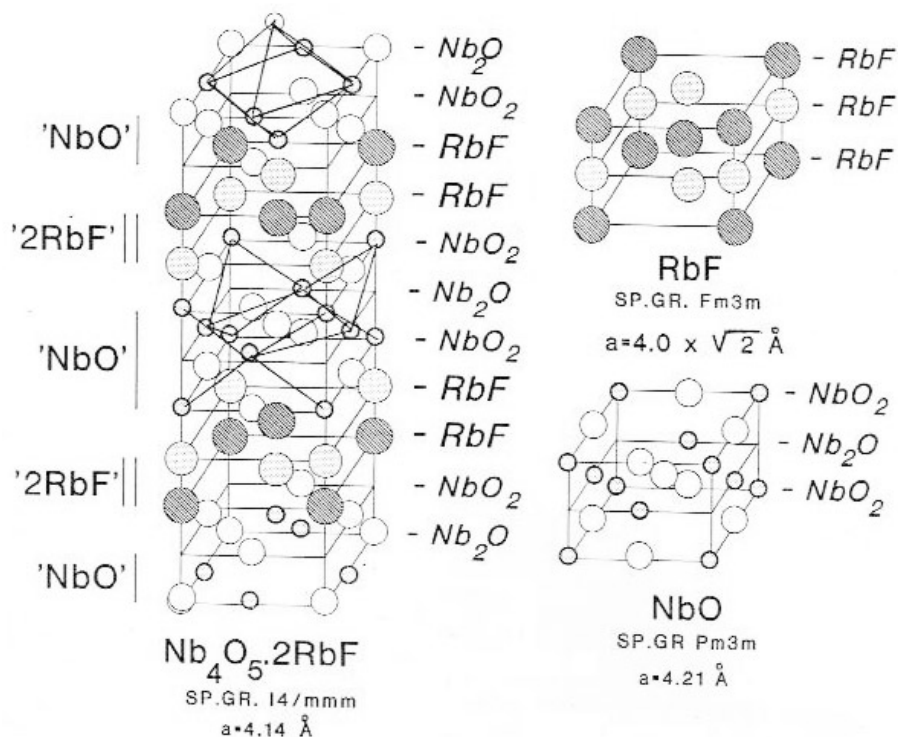


Figure 3. Model of the "NbO" · 2"RbF" composite structure.

and Rb (4.23 Å) (Table 1). This parameter is too small for Li and Na ($a=3.67\text{Å}$) and is too large for Cs (4.44 Å). In both cases, the correspondence between the unit cell parameters of the fragments required to construct a stable layered structure is absent.

Table 1. Parameter a of tetragonal cell calculated for the "NbO" $\times n$ "MeF" ($n=1, 2$) composite structure type on the basis of interatomic distances $d=R\text{Me}^+ + R\text{F}^-$ (R is ionic radius)

Me cation	$d, \text{Å}$	$d, \text{Å}$	$a, \text{Å}$	$a, \text{Å}$
	"NbO" 1"MeF" ($\text{CN}_{\text{Me}} = 12$)	"NbO" 2"MeF" ($\text{CN}_{\text{Me}} = 9$)	"NbO" 1"MeF"	"NbO" 2"MeF"
Na	2.75	2.60	3.89	3.67
K	3.00*	2.91*	4.24*	4.12*
Rb	3.08	2.99*	4.35	4.23*
Cs	3.24	3.14	4.58	4.44

4. Conclusions

It has been shown that the cationic composition of the solvent for niobium complexes is a very efficient tool of controlling the cathodic electrodeposition from melts. Varying the outer-sphere cations composition (along with other parameters of an electrochemical process) allowed to obtain cathodic products of specified chemical and phase composition. Thus, only substitution of sodium and lithium for larger cations in the fluoride solvent with K_2NbOF_5 , led to oxygen content decrease from 14-16 wt % to hundreds of a percent. The definite influence of the solvent cationic composition on the electrochemical synthesis of new niobium compounds was found. The role of outer-sphere cations should be studied also for other metal compounds containing systems, first of all, tantalum, as a niobium analogue.

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