

# The $\text{UO}_2$ - $\text{MeO}_2$ (Me = Th, Pu, Zr) cathode crystalline deposits formation during the melts electrolysis

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## Abstract

The crystalline  $\text{UO}_2$ - $\text{ThO}_2$  (30-50 mol. %),  $\text{UO}_2$ - $\text{PuO}_2$  (6 - 72 mol. %),  $\text{UO}_2$ - $\text{ZrO}_2$  (0.1 - 98 mol. %) cathode deposits were obtained at the electrolysis of the (NaCl-KCl)- $\text{UO}_2\text{Cl}_2$ - $\text{MeCl}_4$  melt, where Me=Th, Pu, Zr. The mechanism of their formation was analyzed. The influence of the  $\text{MeCl}_4$  concentration in the melt and the initial electrolysis current density on the average  $\text{MeO}_2$  concentration in the  $\text{UO}_2$ - $\text{MeO}_2$  cathode deposits was studied. The  $\text{MeO}_2$  fraction concentration decreased consistently as the  $\text{MeCl}_4$  concentration decreased and the electrolysis current density increased. The electrolytic crystalline  $\text{UO}_2$ - $\text{MeO}_2$  cathode deposit is formed by two simultaneous reactions at the electrode: electrolytic reduction of  $\text{UO}_2^{2+}$  to  $\text{UO}_2$  and exchange reaction between  $\text{UO}_2$  and  $\text{Me}^{4+}$  ions, which are present in the molten (NaCl-KCl) - $\text{UO}_2\text{Cl}_2$ - $\text{MeCl}_4$  electrolyte.

*Keywords:* molten salt electrolyte, cathode deposit,  $\text{UO}_2$ - $\text{MeO}_2$  (M=Zr, Th, Pu) system, quantitative composition, structure

## 1. Introduction

The  $\text{UO}_2$  -  $\text{ZrO}_2$ ,  $\text{UO}_2$  -  $\text{ThO}_2$  and  $\text{UO}_2$  -  $\text{PuO}_2$  systems are used as a fuel for nuclear reactors [1]. The latter are of especial interest for the fast-neutron reactors, as large deposits of uranium-238 and thorium are included into the fuel cycle. It is known that uranium dioxide is deposited from the halide melt at the cathode and its density is 10.85 [2], 10.85-10.90 [3] and  $10.92 \pm 0.04$  [4] ( $\text{g}/\text{cm}^3$ ), which is close to the value of the individual dioxide equal to 10.96 [5] ( $\text{g}/\text{cm}^3$ ). The electrolytic method of the  $\text{UO}_2$  -  $\text{MeO}_2$  crystals formation on the cathode in molten salts allows obtaining cathode products, which density is close to the theoretical one. Previously, we have studied the cathode deposits of the  $\text{UO}_2$  -  $\text{ZrO}_2$  heterogeneous system at the (NaCl-KCl)- $\text{UO}_2\text{Cl}_2$ - $\text{ZrCl}_4$  melt electrolysis and the mechanism of their formation has been

suggested [6-9]. They are formed at the simultaneous reactions of the  $\text{UO}_2^{2+}$  ions reduction to  $\text{UO}_2$  and exchange between  $\text{UO}_2$  and  $\text{Zr}^{4+}$  ions, which are present in the salt phase.

The present work analyzed of the possibility to electrocrystallize of homogeneous  $\text{UO}_2 - \text{ThO}_2$  and  $\text{UO}_2 - \text{PuO}_2$  deposits including detection of the maximum content of thorium and plutonium dioxides in these systems. The  $\text{UO}_2 - \text{MeO}_2$  cathode deposits formation mechanism, influence of the electrolysis current density and  $\text{MeCl}_4$  concentration in the  $(\text{NaCl-KCl})\text{-UO}_2\text{Cl}_2\text{-MeCl}_4$  ( $\text{Me} = \text{Zr, Th, Pu}$ ) electrolyte on the deposits structure and composition are studied.

## 2. Mechanism of the $\text{UO}_2 - \text{MeO}_2$ cathode deposits formation

$\text{UO}_2^{2+}$  uranyl ions are the most electropositive components of the salt phase  $(\text{NaCl-KCl})\text{-UO}_2\text{Cl}_2\text{-MeCl}_4$ . As the current passes through the melt the individual phase of uranium dioxide  $\text{UO}_2$  is first extracted at the cathode as the result of the  $\text{UO}_2^{2+}$  uranyl ions reduction



This process takes place at the potential of  $\sim -0.6$  V (relatively to the chlorine reference electrode) [10, 11]. The electrolysis is carried out at the current densities, which do not exceed the limiting diffusion  $\text{UO}_2^{2+}$  ions current. The Zr, Th and Pu extraction potentials are significantly more negative than  $-0.6$  V [12, 13]. That is why zirconium, thorium and plutonium do not appear in the cathode deposit at the electrolysis due to the reduction reaction to their atomic state.

However they appear in the cathode product according to the exchange reaction (2) between the Me (IV) ions, which are present in the molten salts, and uranium dioxide after the formation of the first crystals at the cathode



In fact cations, as shown in equations (1) and (2), are present in the melt as  $[\text{UO}_2\text{Cl}_4]^{2-}$ ,  $[\text{ZrCl}_6]^{2-}$ ,  $[\text{UCl}_6]^{2-}$ , and  $[\text{PuCl}_6]^{2-}$  complex ions [12]; thus, they should be considered in the reaction schemes that define the cathode processes.

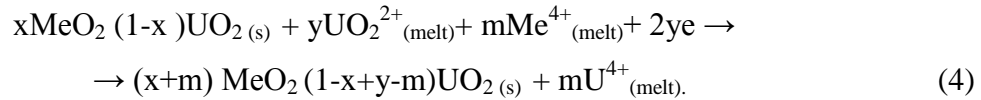
Equations (1) and (2) demonstrate the initial stage of the formation of the solid  $\text{UO}_2\text{-ZrO}_2$  solution at the electrode under a current load. Then  $\text{UO}_2$  crystallizes at the surface of the generated solid  $(1-x)\text{UO}_2 \cdot x\text{ZrO}_2$  solution and uranium dioxide is included in the crystalline lattice. This process is described by equation



The uranyl ions reduction is accompanied by the depolarization [6,11]. The presence of depolarization and appearance of the  $\text{U}^{4+}$  ions in the melt according to the exchange reaction

between the  $\text{Me}^{4+}$  ions and  $\text{UO}_2$  in the  $(\text{NaCl-KCl})\text{-UO}_2\text{Cl}_2\text{-ZrCl}_4$  system under the cathode polarization were experimentally proved [11].

The reduction reaction and the exchange reaction, in which  $\text{Me}^{4+}$  ions interact with uranium dioxide at the surface layer of the growing cathode deposit and not with the individual  $\text{UO}_2$  phase, proceeds simultaneously. This concurrent process of exchange and reduction reactions at the cathode is described by equation



Thus, Eq. (4) is a basic equation, which illustrates the mechanism underlying of the  $\text{UO}_2$  -  $\text{MeO}_2$  deposit formation at the cathode during electrolysis.

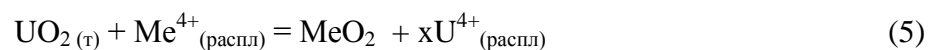
### 3. Quantitative composition of the $\text{UO}_2$ – $\text{MeO}_2$ cathode deposit

The quantitative composition of the cathode deposit depends on the ratio of electrochemical (1) and chemical (2) reaction rates.

The rate of electrochemical reaction (1) is determined by the electrolysis current density. The rate can be easily changed by varying current during the electrolysis. Clearly, larger electrolysis current densities yield higher  $\text{UO}_2$  and lower  $\text{MeO}_2$  concentrations in the cathode deposit under otherwise equal conditions.

The rate of exchange reaction (2) is limited by the diffusion of  $\text{Zr}^{4+}$  ions from the melt bulk to the surface of the cathode deposit. According to Fick's law, diffusion rate is proportional to the zirconium ion concentration in the electrolyte bulk; when diffusion rate is greater, the  $\text{MeO}_2$  concentration is higher and the  $\text{UO}_2$  concentration is lower in the cathode deposit.

The composition of the  $\text{UO}_2$  –  $\text{MeO}_2$  cathode deposit depends on the ratio of electrochemical (1) and chemical (2) reaction rates. The deposits with different oxide concentrations can be generated on the cathode when the reaction rates vary. In addition, the maximum  $\text{MeO}_2$  concentration in the cathode deposit can be determined according to thermodynamic reaction (2). As an initial approximation, a change in the Gibbs energy and the apparent conditional equilibrium constant  $K^*$  for this process can be evaluated using data in literature if zirconium, thorium, and plutonium is assumed to completely substitute for uranium in  $\text{UO}_2$  using equation



for which

$$K^* = K \cdot \gamma_{\text{MeCl}_4} / \gamma_{\text{UCl}_4} = [\text{UCl}_4] / [\text{MeCl}_4] \quad (6)$$

where  $\gamma$  is the activity coefficient with constant value when the component concentration do not exceed 5 mol. % [12]

The thermodynamic data used for individual uranium, zirconium, thorium and plutonium oxides were reported in [14]. The values of the solutions diluted in the electrolyte were used as the values of tetra halides [12]. The values of  $K^*$  in the molten equimolar NaCl – KCl mixture with participation of zirconium, thorium and plutonium tetrachlorides at 1000K were equal to 91, 2.8 and 100, respectively. The equilibrium is seen to be shifted to the right. The values of  $K^*$  for the  $ZrO_2$  and  $PuO_2$  systems were found to be 30 times larger than that for the  $ThO_2$  system. The values of  $K^*$  allowed evaluating the maximum concentrations of zirconium, thorium and plutonium dioxides in the  $UO_2 - MeO_2$  cathode deposit. It was proved that the  $ThO_2$  concentration may reach ~ 75 mol. %, and  $ZrO_2$ ,  $PuO_2$  concentrations are nearly 100 mol. %.

#### 4. Experimental

$UO_2 - MeO_2$  cathode deposits were received under galvanostatic conditions in a hermetic test electrolyzer, which was constructed from quartz and filled with helium. A Pt wire with a diameter of 1 mm was immersed 12 mm deep into the melt ( $S = 0.4 \text{ cm}^2$ ) and served as the cathode. A carbon electrode was separated from the electrolyte by a porous asbestos diaphragm and served as the anode. The electrolyzer, the electrolyte technique, and the method for analyzing the salt phase have been described elsewhere [7,9]. The amount of electricity consumed for one deposit was constant for each test and was 0.25 A·h. The mass of the electrolyte was approximately 100 g. The obtained cathode deposits were studied by chemical, X-ray phase analysis and X-ray spectral microanalysis.

#### 5. Results and discussion

##### 5.1. Influence of the $MeCl_4$ concentration

The influence of the  $MeCl_4$  concentration was studied at  $UO_2-ZrO_2$  cathode deposit formation during (NaCl–KCl) -  $UO_2Cl_2-ZrCl_4$  melt electrolysis. The  $ZrCl_4$  concentration in the melt was varied from 0.1 to 12.3 wt. %.

Figure 1 shows the dependence of the average  $ZrO_2$  concentration in the  $ZrO_2-UO_2$  cathode deposit on the  $ZrCl_4$  concentration in the molten electrolyte.

As expected, the average  $ZrO_2$  concentration in the cathode product increased as the  $ZrCl_4$  concentration in the molten salt increased. The increased rate of the exchange reaction (2) and the corresponding increase in zirconium concentration, which transfers to the oxide phase

during electrolysis under otherwise equal conditions, results in the increasing ZrO<sub>2</sub> content in the cathode deposit and the increasing ZrCl<sub>4</sub> concentration in the electrolyte.

### 5.2. Influence of the electrolysis current density

The influence of the electrolysis current density was studied at UO<sub>2</sub>-ZrO<sub>2</sub> and UO<sub>2</sub>-ThO<sub>2</sub> cathode deposits formation. The initial electrolysis current density was varied from 0.04 to 0.63 A/cm<sup>2</sup> at a fixed molten salt composition.

In each case, the MeO<sub>2</sub> concentration in the UO<sub>2</sub>-ZrO<sub>2</sub> and UO<sub>2</sub>-ThO<sub>2</sub> cathode deposits decreased as the electrolysis current density increased. Figure 2 shows the typical change in average zirconium and thorium dioxides concentration for the solid phase.

The ZrO<sub>2</sub> and ThO<sub>2</sub> concentrations in the cathode deposits decreased as the electrolysis current density increased because the rate of the UO<sub>2</sub><sup>2+</sup> ions reduction to UO<sub>2</sub> increased. Thus, the UO<sub>2</sub> fraction in the cathode deposit and the cathode deposit weight increased under otherwise equal conditions, whereas the zirconium and thorium dioxides concentration decreased. The thorium dioxide content equal to 50 mol. % is the maximum. As the electrolysis initial current density decreased from 0.08 to 0.04 A/cm<sup>2</sup>, the ThO<sub>2</sub> concentration in the oxide phase was expected to increase as the rate of the electrochemical reaction decreased. However, the cathode deposit composition remained unchanged. In this case only a half of uranium dioxide was changed by thorium dioxide, which we assume to be due to the thermodynamics of the exchange reaction between UO<sub>2</sub> and thorium tetrachloride.

The results obtained agree with the literature data on the exchange reaction between UO<sub>2</sub> and Th<sup>4+</sup> ions in the chloride media [15].

### 5.3. Structure and phase composition of the UO<sub>2</sub>-MeO<sub>2</sub> cathode deposits

#### 5.3.1. UO<sub>2</sub>-ZrO<sub>2</sub> cathode deposits

The UO<sub>2</sub>-ZrO<sub>2</sub> cathode deposits, which contained up to 98 mol. % ZrO<sub>2</sub>, were formed. From one to three phases were detected in the deposits depending on the uranium oxide and zirconium concentrations: a cubic phase based on UO<sub>2</sub>, a monoclinic phase based on ZrO<sub>2</sub>, and tetragonal phase based on ZrO<sub>2</sub>. The uranium and zirconium concentrations in these three phases were defined using the Camebax electron probe microanalyzer (Table 1).

**Table 1**

Phases in the UO<sub>2</sub>-ZrO<sub>2</sub> system and UO<sub>2</sub> and ZrO<sub>2</sub> concentrations in them

	Concentration, mol.%
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Phases	ZrO <sub>2</sub>			UO <sub>2</sub>		
	Our data	Literature data		Our data	Literature data	
		[17,18]	[19]		[17,18]	[19]
Cubic	0 – 5	0 – 15	0 - 10	95 – 100	85-100	90 - 100
Tetragonal	73 – 77	86-97	~ 80	23 – 27	3-14	~ 20
Monoclinic	85 – 90	97 - 100	~ 90 - 100	10 – 15	0-3	~ 0-10

### 5.3.2. UO<sub>2</sub>–ThO<sub>2</sub> cathode deposits

The UO<sub>2</sub>–ZrO<sub>2</sub> cathode deposits, which contained up to 50 mol. % ThO<sub>2</sub>, were formed. The ThO<sub>2</sub> concentration of 50 mol.% is maximum under our experimental conditions. All deposits were found to be crystalline, single phase cubic solid UO<sub>2</sub> - ThO<sub>2</sub> solutions. Their crystalline lattice parameter increased naturally as the average concentration of thorium dioxide in the cathode deposit grew.

In the oxide phases containing less than 50 mol. % of ThO<sub>2</sub>, the ThO<sub>2</sub> concentration at first increased in direction from the inner layers to the outer ones and when the maximum concentration of 50 mol. % was reached it remained unchanged.

The increase in the ThO<sub>2</sub> concentration in the oxide phase (Fig. 3a) is due to the changes in the ratios of reduction and exchange reactions during the electrolysis. The experimentally found uranium and thorium distribution in the cathode deposit in the direction from the inner layers to the outer ones proves that the reduction reaction rate decreases faster than that of the exchange reaction.

In the cathode deposits containing 50 mol. % of UO<sub>2</sub> and 50 mol. % of ThO<sub>2</sub> the uranium and thorium radiation intensities were close and remained constant. Their values correspond to Fig. 3b.

### 5.3.3. UO<sub>2</sub>–PuO<sub>2</sub> cathode deposits

UO<sub>2</sub>–PuO<sub>2</sub> cathode deposits were formed under chlorine atmosphere to preserve Pu (IV) in the melt. The equimolar NaCl-KCl, NaCl-CsCl and eutectic LiCl-KCl mixtures served as solvents. The UO<sub>2</sub>Cl<sub>2</sub> and plutonium chloride concentrations in them were about 6 and 2 mol. % respectively. Two cathode deposits were subsequently formed using the same original electrolyte. Table 2 presents the electrolysis conditions and its results.

**Table 2**

Electrolysis conditions and UO<sub>2</sub>–PuO<sub>2</sub> cathode deposits composition

Electrolysis conditions	Cathode deposit
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Solvent	Deposit	T, °C	i, A/cm <sup>2</sup>	Time, h	PuO <sub>2</sub> , mol. %	Phase composition	Lattice parameter UO <sub>2</sub> -PuO <sub>2</sub> , m • 10 <sup>8</sup>
NaCl-KCl	1	730	0,07	6	72	PuO <sub>2</sub> UO <sub>2</sub> -PuO <sub>2</sub>	5.465 ± 0.001
	2		0,06	3	42		
NaCl-CsCl	1	550	0,07	6	≈ 6	UO <sub>2</sub> -PuO <sub>2</sub>	5.4655 ± 0.0006
	2		0,06	3			
LiCl-KCl	1		0,07	6			
	2		0,06	3			

## 6. Conclusion

1. The mechanism of the UO<sub>2</sub>-MeO<sub>2</sub> cathode deposits electrocrystallization at the halide (NaCl-KCl) -UO<sub>2</sub>Cl<sub>2</sub>-MeCl<sub>4</sub> melt electrolysis, where Me=Th, Pu, Zr, was analyzed. Deposits were found to form as the results of the simultaneous reactions of the UO<sub>2</sub><sup>2+</sup> ions electrolytic reduction to UO<sub>2</sub> and the exchange between UO<sub>2</sub> and Me<sup>4+</sup> ions, which are present in the molten electrolyte.
2. The MeO<sub>2</sub> fraction in the UO<sub>2</sub>-MeO<sub>2</sub> cathode deposits was seen to decrease naturally as the MeCl<sub>4</sub> concentration decreased and the current density increased.
3. The UO<sub>2</sub>-ZrO<sub>2</sub> (0.1 - 98 mol. %), UO<sub>2</sub>-ThO<sub>2</sub> (30 - 50 mol. %), UO<sub>2</sub>-PuO<sub>2</sub> (6 - 72 mol. %) crystalline cathode deposits were obtained.
4. The chemical and phase compositions of cathode deposits were determined.

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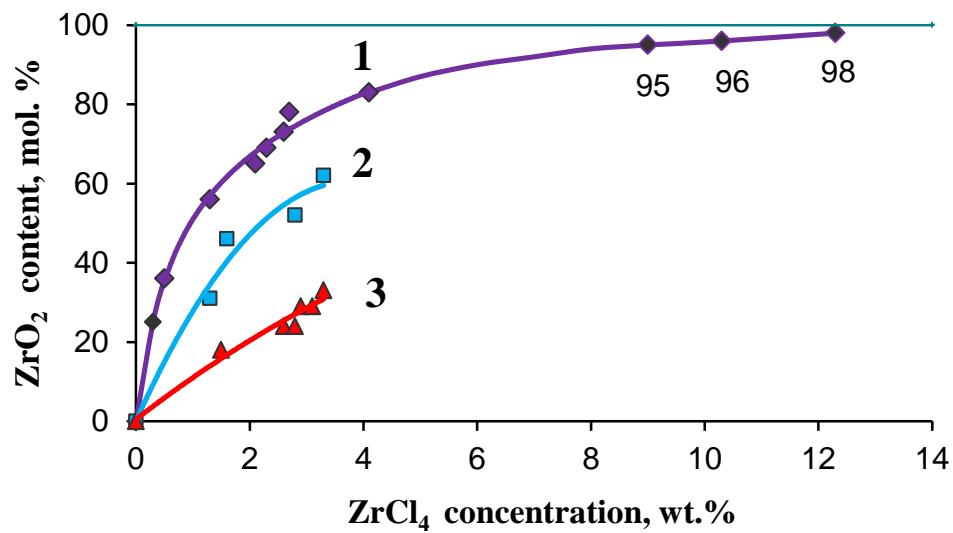


Fig. 1

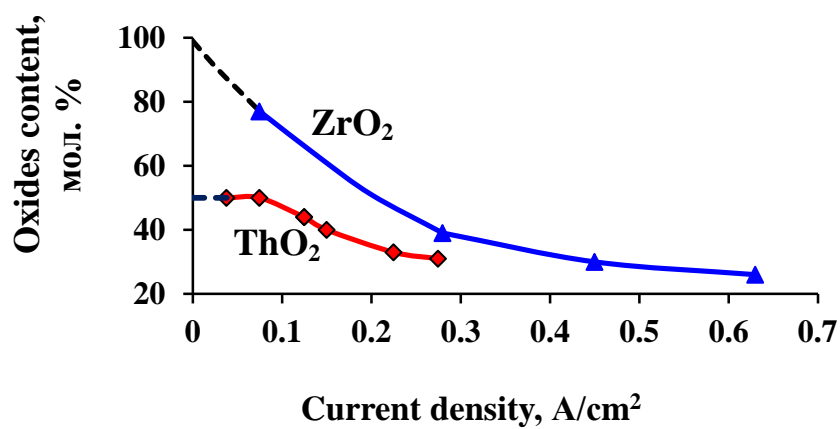


Fig. 2

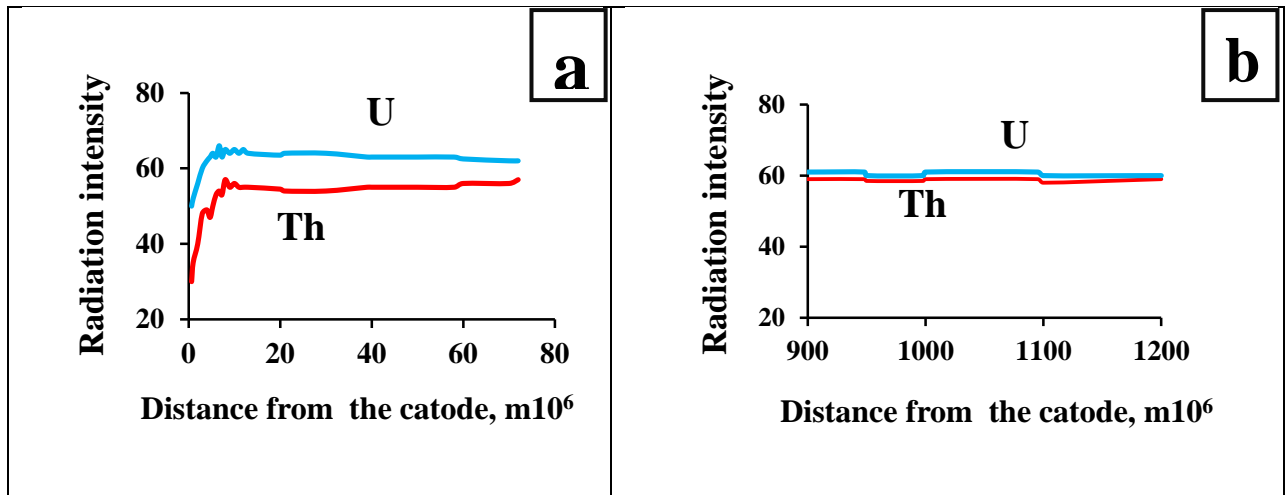


Fig. 3

### Captions to illustration

Fig.1. Influence of the  $ZrCl_4$  concentration in the  $NaCl-KCl-UO_2Cl_2-ZrCl_4$  melt on the average  $ZrO_2$  content in the  $ZrO_2-UO_2$  cathode deposits

- 1- 750 °C, 0,08 A/cm<sup>2</sup>,  $UO_2Cl_2$  ~12 wt.%
- 2- 700 °C, 0,28 A/cm<sup>2</sup>,  $UO_2Cl_2$  ~10 wt.%,
- 3- 750 °C, 0,63 A/cm<sup>2</sup>,  $UO_2Cl_2$  ~27 wt.%.

Fig.2. Influence of the electrolysis current density on the average  $ZrO_2$  and  $ThO_2$  content in the  $UO_2-MeO_2$  cathode deposit, 750 °C.

Melt, mol. %:  $(NaCl-KCl)-UO_2Cl_2$  (3) –  $ThCl_4$  (3.5),  $(NaCl-KCl)-UO_2Cl_2$  (3) –  $ZrCl_4$  (1.4)

Fig.3. Distribution of uranium and thorium along the  $UO_2-ThO_2$  cathode deposit bulk. Average  $ThO_2$  composition is 40 mol. %.

