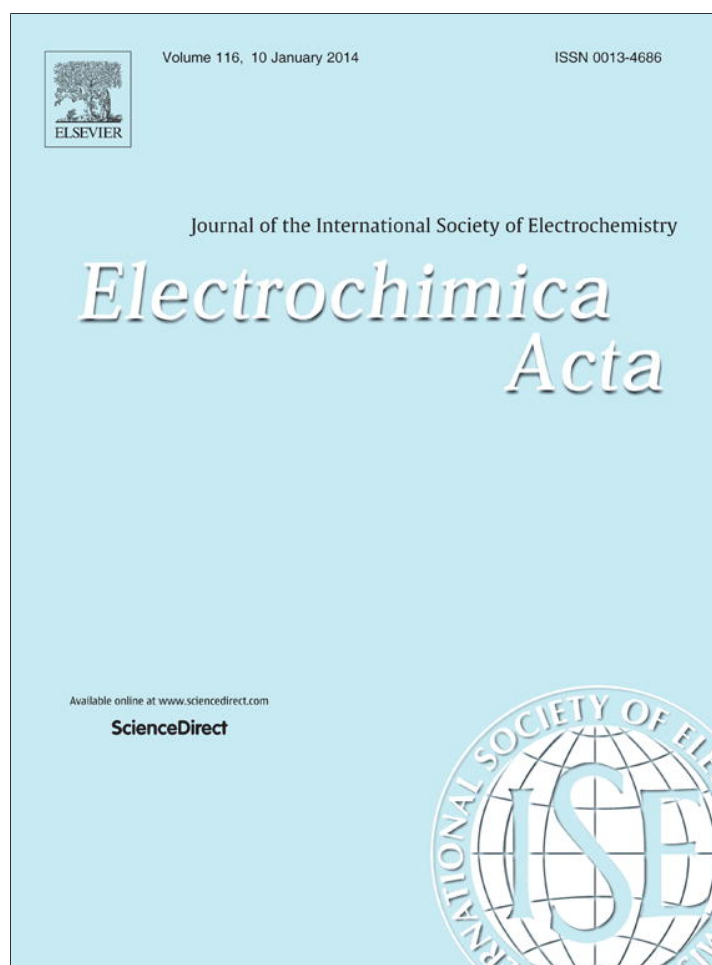


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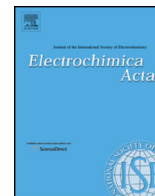
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Regularities of cathode deposit formation during simultaneous reduction and exchange reactions. Influence of the electrolysis conditions on the concentration of components in the $\text{UO}_2\text{-ZrO}_2$ cathode deposit

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ABSTRACT

This paper represents the experimental data on a quantitative composition of cathode $\text{UO}_2\text{-ZrO}_2$ deposits, which are formed through simultaneous electrolytic reduction of UO_2^{2+} ions to UO_2 and the exchange between the UO_2 and Zr^{4+} ions present in the molten $(\text{NaCl-KCl})_{\text{equim.}}\text{-UO}_2\text{Cl}_2\text{-ZrCl}_4$ electrolyte. A scheme for the formation of $\text{UO}_2\text{-ZrO}_2$ deposits containing up to 98 mol. % of ZrO_2 is provided.

The fraction of zirconium dioxide decreased as the ZrCl_4 concentration decreased and as current density and electrolysis times increased. The electrolyte temperature influence on the average composition of the $\text{UO}_2\text{-ZrO}_2$ deposit was found to be insignificant. The structure of the cathode deposit was analyzed.

The established regularities are explained by the change in the reduction and exchange reaction rates at the cathode.

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1. INTRODUCTION

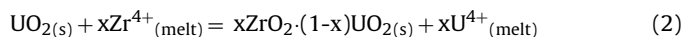
The regularities of cathode deposit formation during simultaneous reduction and exchange reactions will be considered in a series of articles on $\text{UO}_2\text{-Me}_x\text{O}_y$ (Me = Zr, Nb, Th) oxide production at the cathode from a $(\text{NaCl-KCl})_{\text{equim.}}\text{-UO}_2\text{Cl}_2\text{-MeCl}_n$ melt. The major experimental tests were performed through $\text{UO}_2\text{-ZrO}_2$ deposit electrocrystallization. This system was studied in detail between 1950 and 1960 [1]. Renewed interest in this research arose after the Chernobyl NPP tragedy. Currently, research is performed by Russian, European, Canadian, Japanese and American scientists to predict the behavior of nuclear fuel in heavy NPP accidents [2–11]. The characteristics are studied in detail using the $\text{UO}_2\text{-ZrO}_2$ system because the equilibrium constant for the uranium dioxide and zirconium chloride exchange reaction is intermediate compared with those of the uranium dioxide–thorium chloride and uranium dioxide–niobium chloride exchange reactions.

Only two articles [12,13] in literature describe the production of $\text{UO}_2\text{-ZrO}_2$ deposits at cathodes. In both cases, they were deposited

from a $(\text{NaCl-KCl})_{\text{equim.}}\text{-UO}_2\text{Cl}_2\text{-ZrCl}_4$ melt. In accordance with equation (1), the electrochemical reduction of uranyl ions to crystalline uranium dioxide at an inert cathode is the initial stage of the process:



The next stage is an exchange reaction between uranium dioxide, which is formed at the cathode, and Zr^{4+} ions in the melt that forms a solid solution according to equation (2):



During this reaction, the Zr^{4+} ions are not electrochemically active. The reduction potentials for Zr(IV) to Zr(II) and then to metallic zirconium are 1.0 or 1.5 V more negative than the potential for uranium dioxide deposition at the cathode at equal concentrations in the molten NaCl–KCl electrolyte [14]. Researches have empirically demonstrated that Zr^{4+} ions disappear and U^{4+} ions appear upon Pt cathode polarization in the NaCl–KCl melt that contains 0.3 mol% UO_2Cl_2 and 0.3 mol. % ZrCl_4 [12].

In fact, cations, as shown in equations (1) and (2), are present in the melt as $[\text{UO}_2\text{Cl}_4]^{2-}$, $[\text{ZrCl}_6]^{2-}$, and $[\text{UCl}_6]^{2-}$ complex ions [14]; thus, they should be considered in the reaction schemes that define the cathode processes.

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The quantitative composition of the cathode deposit depends on the ratio of electrochemical (1) and chemical (2) reaction rates. The $\text{UO}_2\text{-ZrO}_2$ solid solution with different oxide concentrations can be generated on the cathode when the reaction rates vary. In addition, the maximum ZrO_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 apparent equilibrium constant for this process can be evaluated using data in literature if zirconium is assumed to completely substitute for uranium in UO_2 using equation (3):



The equilibrium of this reaction is shifted to right. The value of the apparent equilibrium constant for reaction (3) is $k^* = [\text{UCl}_4]/[\text{ZrCl}_4] = k \cdot \gamma_{\text{ZrCl}_4}/\gamma_{\text{UCl}_4}$, which was calculated for the $(\text{NaCl-KCl})_{\text{equim}}$ melt using literature data [14–16] and is equal to 170 at 973 K. The γ -terms denote the activity coefficients with constant values when the zirconium and uranium tetrachloride concentrations do not exceed several mole percent [14]. The empirically derived ratio of the mole-fraction of zirconium tetrachloride to the uranium tetrachloride concentration was approximately 100.

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 UO_2 and lower ZrO_2 concentrations in the solid solution under otherwise equal conditions.

The rate of reaction (2) is limited by the rate of transfer of Zr^{4+} ions the cathode deposit surface or the rate of removal of U^{4+} ions from the surface to the electrolyte bulk.

The literature contains no data related to the diffusion coefficients of Zr^{4+} and U^{4+} ions in alkali halide melts with uranyl halogenides; data are only available for salts without UO_2Cl_2 . The diffusion coefficients for the Zr^{4+} and U^{4+} ions in the molten equimolar NaCl-KCl mixture are consistent within the experimental error [17,18]. Thus, their values are 2.6×10^{-5} and 2.5×10^{-5} at 1000 K and 4.2×10^{-5} and 4.4×10^{-5} $\text{cm}^2 \text{s}^{-1}$ at 1100 K, respectively. Uranyl chloride in the melt may affect these values. However, if the diffusion coefficients for these ions change, they change in an equivalent manner.

Given the apparent equilibrium constant for zirconium in reaction (3), which is in the proximal electrode layer as Zr^{4+} , it entirely transfers to the cathode deposit. Considering this transfer and the fact that the diffusion coefficients for the Zr^{4+} and U^{4+} ions are equal, the rate of exchange reaction (2) is limited by the diffusion of 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 ZrO_2 concentration is higher and the UO_2 concentration is lower in the solid solution.

The continuous formation of the solid $\text{ZrO}_2\text{-UO}_2$ solution at the cathode represents a special class of electrochemical reaction accompanied by an exchange reaction between the growing cathode deposit and an additional electrochemically inactive electrolyte component. Additional studies [12,13,19] have described similar reactions. Work [19] reports the production of $\text{UO}_2\text{-ThO}_2$ cathode deposits in a LiCl-KCl melt with gaseous HCl . The thorium dioxide concentration was (2–54) wt.%; additional information on this process was not provided. Two other studies were performed at the Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences (IHTE UB RAS). The first study [12] describes UO_2 deposit production with 3 and 6 mol. % ZrO_2 and NbO_2 , respectively, and demonstrates that the uranium dioxide crystalline lattice parameter depends on the oxide composition. The second publication [13] provides additional information. The influence of the $\text{NaCl-KCl-UO}_2\text{Cl}_2\text{-ZrCl}_4\text{-UCl}_4$ melt component concentrations on the quantitative $\text{ZrO}_2\text{-UO}_2$ oxide phase

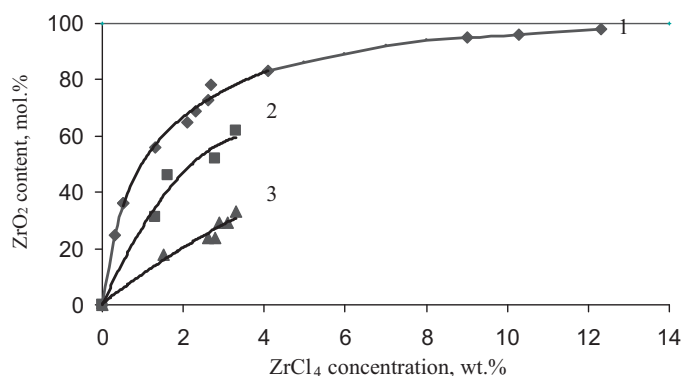


Fig. 1. Influence of the ZrCl_4 concentration in the $\text{NaCl-KCl-UO}_2\text{Cl}_2\text{-ZrCl}_4$ melt on the average ZrO_2 content in the $\text{ZrO}_2\text{-UO}_2$ cathode deposits.

1- 750 °C, 0,08 A cm⁻², C(UO₂Cl₂) ~12 wt.%,

2- 700 °C, 0,28 A cm⁻², C(UO₂Cl₂) ~10 wt.%,

3- 750 °C, 0,63 A cm⁻², C(UO₂Cl₂) ~27 wt.%,

composition was studied. The cathode deposits generated during the study contained more than 90 mol. % ZrO_2 .

The aim of this work is to determine the influence of the electrolysis conditions on the average composition of the $\text{ZrO}_2\text{-UO}_2$ deposit during simultaneous electrolytic reduction and exchange reactions between the cathode deposit and the electrolyte.

2. EXPERIMENTAL

$\text{ZrO}_2\text{-UO}_2$ cathode deposits were reduced 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 [13].

The amount of electricity consumed for one deposit was constant for each test and was 0.25 A·h, apart from the tests on long-term electrolysis effects. 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.

The average U and Zr concentrations in cathode product were defined by chemical method [20,21]. Cathode deposit phase composition was studied by DRON-2 diffractometer at copper K_{α} emission with nickel filter. The X-ray spectral microanalysis was performed by Camebax device. Metallic zirconium and zirconium dioxide and uranium dioxide were used as a reference standard. Crystalline uranium dioxide was obtained from the $(\text{NaCl-KCl})_{\text{equim}}\text{-UO}_2\text{Cl}_2$ melt (without ZrCl_4 additions).

3. RESULTS AND DISCUSSION

3.1. Influence of the ZrCl_4 concentration

The influence of the ZrCl_4 concentration was studied at 700 and 750 °C for the initial current density interval of 0.08 to 0.63 A cm⁻². The ZrCl_4 concentration in the melt was varied from 0.1 to 12.3 wt.%. The uranyl chloride concentration was 8–32 wt. % and remained unchanged in each series of experiments.

Fig. 1 shows the dependence of the average ZrO_2 concentration in the $\text{ZrO}_2\text{-UO}_2$ 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

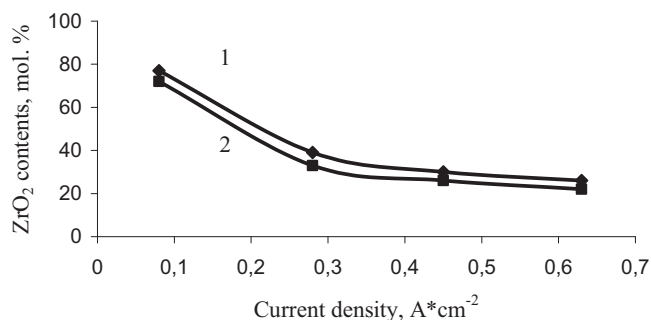


Fig. 2. Dependence of the electrolysis current density on the average ZrO_2 content in the UO_2-ZrO_2 cathode deposit. $(NaCl-KCl)_{equim.}-UO_2Cl_2(30\text{ wt.}\%)-ZrCl_4$
1- 750 °C, $C(ZrCl_4) = 3.6\text{ wt.}\%$, 2- 700 °C, $C(ZrCl_4) = 3.1\text{ wt.}\%$

increased. A relatively rapid composition change for the ZrO_2-UO_2 cathode deposit was observed with the addition of small quantities of $ZrCl_4$ to the electrolyte. As $ZrCl_4$ concentration further increased, the rate of the composition change of the ZrO_2-UO_2 solid solution decreased.

The maximum ZrO_2 concentration in the oxide phase under the experimental conditions was 98 mol. %. A deposit with such a composition was formed on the cathode when the electrolysis current density was 0.08 $A\text{ cm}^{-2}$ and the $ZrCl_4$ concentration was 12.3 wt. %.

The increased rate of exchange reaction (2) and the corresponding increase in zirconium, which transfers to the oxide phase during electrolysis under otherwise equal conditions, results in the increasing ZrO_2 content in the cathode deposit and the increasing $ZrCl_4$ concentration in the electrolyte.

3.2. Influence of the electrolysis current density

The initial electrolysis current density was varied from 0.08 to 0.63 $A\text{ cm}^{-2}$ at a fixed molten salt composition.

In each case, the ZrO_2 concentration in the UO_2-ZrO_2 cathode deposits decreased as the electrolysis current density increased. Fig. 2 shows the typical change in average zirconium dioxide concentration for the solid phase.

The strongest influence of the current density on the quantitative cathode deposit composition was observed at current densities less than 0.3 $A\text{ cm}^{-2}$. The rate of change in the oxide concentrations for the solid solution then decreased.

The ZrO_2 concentration in the UO_2-ZrO_2 cathode deposits decreased as the electrolysis current density increased because the reduction rate for UO_2^{2+} ions to UO_2 increased. Thus, the UO_2 fraction in the cathode deposit and the cathode deposit's mass increased under otherwise equal conditions, whereas the zirconium dioxide concentration decreased.

As expected, the $ZrCl_4$ concentration in the melt decreased during electrolysis, and UCl_4 was formed. Fig. 3 shows the dependence of such electrolyte values on the current density after electrolysis.

In cases where the electrolysis current density was greater, more $ZrCl_4$ remained in the melt after electrolysis and less uranium tetrachloride was formed. Maximum changes were observed at low electrolysis current densities when ZrO_2 -enriched deposits were formed at the cathode.

3.3. Influence of temperature

The studies were performed at 700, 750, and 790 °C and at two limiting values for the electrolysis current density (0.08 and 0.63 $A\text{ cm}^{-2}$). In the melt, the UO_2Cl_2 concentration was 27 wt. %, and the zirconium tetrachloride concentration was approximately 3 wt. %.

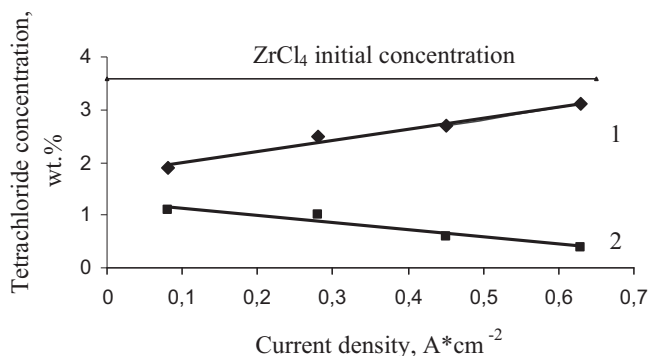


Fig. 3. Influence of the electrolysis current density on the uranium and zirconium tetrachloride concentrations in the $(NaCl-KCl)_{equim.}-UO_2Cl_2(32\text{ wt.}\%)-ZrCl_4(3.6\text{ wt.}\%)$ melt after the electrolysis termination at 750 °C. 1- $ZrCl_4$, 2- UCl_4

Fig. 4 shows the effect of temperature on the average ZrO_2 concentrations in the UO_2-ZrO_2 cathode deposits.

During the oxide phase, the ZrO_2 concentration increased insignificantly as the temperature was increased at the electrolysis current density of 0.63 $A\text{ cm}^{-2}$. The ZrO_2 concentration remained almost unchanged at temperatures less than 750 °C and at the current density of 0.08 $A\text{ cm}^{-2}$ and then slightly decreased.

Temperature influences the cathode deposit composition either through changes in the Zr^{4+} ion diffusion coefficients or the UO_2 current efficiency. We estimated their potential influence on the ZrO_2 concentration in the UO_2-ZrO_2 cathode deposits.

The literature contains published values for the Zr^{4+} ion diffusion coefficients in a molten equimolar $NaCl-KCl$ mixture [17]. If we assume that the addition of UO_2Cl_2 to a concentration of 7 mol. % in the electrolyte, which corresponds to the conditions herein, does not influence the diffusion of Zr^{4+} ions, then the Zr^{4+} ion diffusion coefficients increase from 2.3×10^{-5} to 3.0×10^{-5} and $3.6 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ as the temperature is increased from 700 to 750 and 790 °C, respectively [17]. Thus, the zirconium mass in the cathode deposit should increase under otherwise equal conditions.

The current efficiency remained almost unchanged. The maximum change in the current efficiency was 8%; hence, this change in current efficiency was neglected in the calculations.

The ZrO_2 concentration in deposits formed at 700 °C was used as a reference value. The ZrO_2 concentration in the oxide phase at 750 °C and 790 °C was calculated using equation (4):

$$C_t = D \cdot C_{700} / [D \cdot C_{700} + (1 - C_{700})] \quad (4)$$

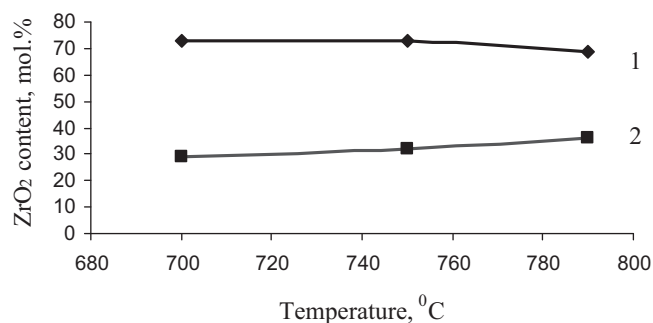


Fig. 4. Influence of the temperature on the average ZrO_2 content in the UO_2-ZrO_2 cathode deposits. $(NaCl-KCl)_{equ.}-UO_2Cl_2(27\text{ wt.}\%)-ZrCl_4$
1- 0.08 $A\text{ cm}^{-2}$, $C(ZrCl_4) = 3.1\text{ wt.}\%$
2- 0.63 $A\text{ cm}^{-2}$, $C(ZrCl_4) = 3.3\text{ wt.}\%$

where C is the molar-fraction ZrO_2 concentration in the cathode deposit, D is the ratio between the Zr^{4+} diffusion coefficient at temperature t and the Zr^{4+} diffusion coefficient at 700 °C.

The calculation results are presented in Table.

The calculated values are larger than the experimental values; the difference between the values increased as the temperature was increased. However, the experimental values are assumed to fit the calculated values for the ZrO_2 concentration in the solid solution. Thus, the maximum deviations of the calculated results from the experimental results were observed for experiments conducted at 790 °C and did not exceed 14 and 19% at electrolysis current densities of 0.63 and 0.08 A cm⁻², respectively.

The calculated values deviated from the experimental values at temperatures greater than 700 °C, with even a small decrease in the ZrO_2 concentration in the cathode deposit at 790 °C and an electrolysis current density of 0.1 A cm⁻² due to the volatility of $ZrCl_4$ in molten salts. The volatility is known to increase exponentially as the electrolyte temperature is increased [22], whereas the concentration of $ZrCl_4$ in the melt decreases with increasing temperature. The ZrO_2 concentration in the cathode deposit was calculated using equation (4) without consideration of changes in the $ZrCl_4$ concentrations; thus, the calculated results were slightly enhanced as compared with the experimentally derived values.

The $ZrCl_4$ is volatilized because the concentration of zirconium dioxide decreases in the solid UO_2-ZrO_2 solution at 790 °C. When equal amount of electricity was used to produce each deposit, the electrolysis duration increased from 1 to 8 hours as the initial current density was changed from 0.63 to 0.08 A cm⁻². In fact, longer electrolysis times resulted in a greater degree of $ZrCl_4$ evaporation; thus, we expected to observe maximum $ZrCl_4$ depletion from the electrolyte at 0.08 A cm⁻² and 790 °C. The exchange reaction takes place at lower $ZrCl_4$ concentrations. Thus, the ZrO_2 concentration in the cathode deposit at 790 °C is lower than that at 700 °C despite the enhanced Zr^{4+} ion diffusion coefficients.

Therefore, as the temperature is increased, the quantitative composition for the cathode UO_2-ZrO_2 deposit changes with an increase in the Zr^{4+} ion diffusion coefficients in the electrolyte and in the $ZrCl_4$ volatility. In addition, the influence of the $ZrCl_4$ volatility increases as temperature increases and as electrolysis current density decreases; in the latter case, the increased influence of $ZrCl_4$ volatility is due to prolonged electrolysis.

3.4. Influence of electrolysis duration

In these studies, we varied the electrolysis duration by increasing the deposition time for one deposit. Otherwise, three cathode deposits were subsequently formed from the same electrolyte. In addition, the amount of current that passed through the melt increased by a factor of three. Current of 0.25 A-hour was consumed for generation of each deposit.

3.4.1. Influence of electrolysis time

During the experiments to evaluate the effects of electrolysis time, the electrolysis duration was varied from 2.3 to 7.5 hours under otherwise equal conditions. These experimental data are provided in Fig. 5.

The average concentration of ZrO_2 in the cathode deposit decreased with longer electrolysis times due to the decreased $ZrCl_4$ concentration in the electrolyte. Fig. 6 shows the concentration of $ZrCl_4$ in the melt after the process was terminated. For longer electrolysis processes, the $ZrCl_4$ concentration was lower in the salt phase (curve 2). Therefore, the amount of zirconium transferred to the cathode deposit per unit of time decrease in cases where the concentrations of deposited UO_2 remain unchanged. Thus, both the ZrO_2 concentration in the outer layer and the

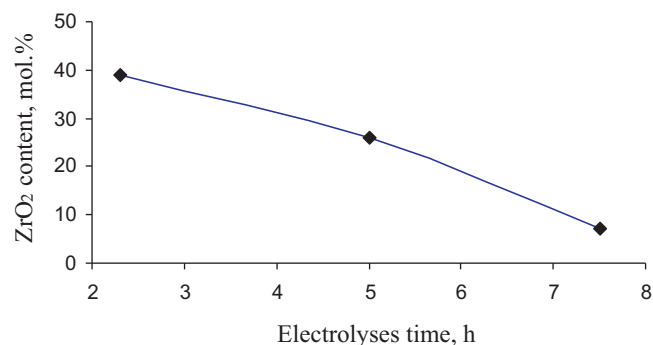


Fig. 5. Influence of the electrolysis duration on the average ZrO_2 content in the cathode UO_2-ZrO_2 deposits:

(NaCl-KCl)equim - UO_2Cl_2 (26 wt. %)- $ZrCl_4$ (3.3 wt. %) 750 °C, 0.28 A cm⁻²

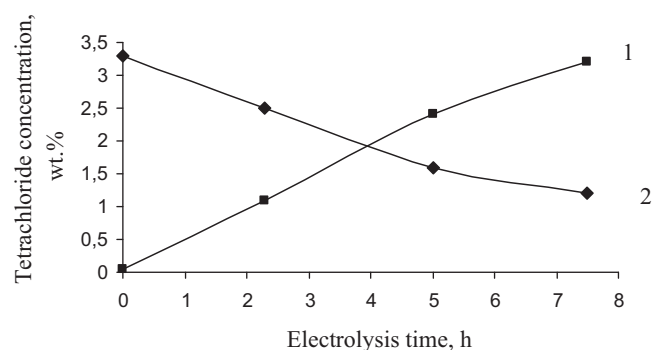


Fig. 6. Influence of the electrolysis duration on the zirconium and uranium tetrachloride concentration after the electrolysis.

(NaCl-KCl)equim - UO_2Cl_2 (26 wt. %)- $ZrCl_4$ (3.3 wt. %), 750 °C, 0.28 A cm⁻²
1 - UCl_4 , 2 - $ZrCl_4$

average UO_2-ZrO_2 concentration should decrease as compared with the previous observations.

The concentration of UCl_4 , which is generated in the melt from the exchange reaction between UO_2 and $ZrCl_4$, increased in the salt phase during electrolysis (curve 1).

3.4.2. Influence of current density

The experiments were performed using different component concentrations, current densities, and temperatures.

Fig. 7 shows the average ZrO_2 concentration for each of three deposits as a function of the current that was passed through the melt. The concentrations of UCl_4 and $ZrCl_4$ in the molten salt are

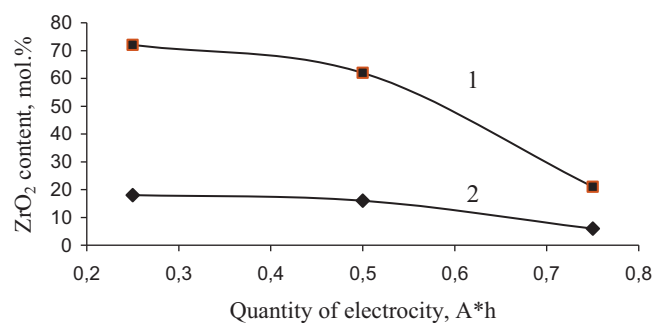


Fig. 7. Influence of the quantity of electricity passed through the melt on the average ZrO_2 concentration in the cathode ZrO_2-UO_2 deposits (subsequent generation of three deposits).

Initial melt: (NaCl-KCl)equim - UO_2Cl_2 (26 wt. %)- $ZrCl_4$ (3.2 wt. %), 750 °C, 1 - 0.08 A cm⁻², 2 - 0.45 A cm⁻²

Table 1

| No. | Current density, A cm ⁻² | ZrO ₂ concentration in the cathode deposit, mol% | | | | |
|-----|-------------------------------------|---|-----|--------|-----|--------|
| | | 700 °C | | 750 °C | | 790 °C |
| | | exp | exp | calc | exp | calc |
| 1 | 0.08 | 73 | 73 | 78 | 69 | 81 |
| 2 | 0.63 | 29 | 32 | 35 | 36 | 39 |

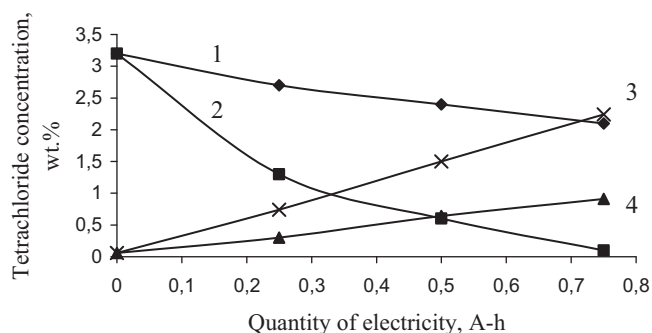


Fig. 8. Influence of the quantity of electricity passed through the melt on the zirconium and uranium tetrachloride concentration in the melt after the electrolysis. (subsequent generation of three deposits). Initial melt: (NaCl-KCl) equim – UO₂Cl₂ (26 wt.%) – ZrCl₄ (3.2 wt. %), 750 °C. 1,2 – ZrCl₄, 3,4 – UCl₄, 1,4 – 0.45 A cm⁻², 2,3 – 0.08 A cm⁻²

shown in Fig. 8. The melt probes were collected after each deposition.

The ZrO₂ concentration decreased in each subsequent deposit because electrolysis began with a lower ZrCl₄ concentration in the salt phase when the first deposit was generated (curves 1, 2). The exchange reaction between UO₂ and ZrCl₄ resulted in a consistent increase in the UCl₄ concentration in the melt (curves 3, 4).

Thus, the ZrO₂ concentration decreased in the UO₂–ZrO₂ cathode product during electrolysis upon forming one or several deposits.

3.5. Structure of UO₂–ZrO₂ cathode deposits.

The structure of several UO₂–ZrO₂ cathode deposits was studied. The average zirconium dioxide concentration in them did not exceed 90 mol. %. Each deposit was found to include from one to three phases: UO₂-based cubic phase, ZrO₂-based monoclinic phase and ZrO₂-based tetragonal phase. These three phases are present on the UO₂–ZrO₂ system phase diagram [1,23–25].

In deposits with the ZrO₂ concentration not exceeding 6 mol.% only a cubic phase was observed by the X-ray phase analysis. This phase has a layered structure (Fig. 9), which is not present in individual crystalline uranium dioxide.

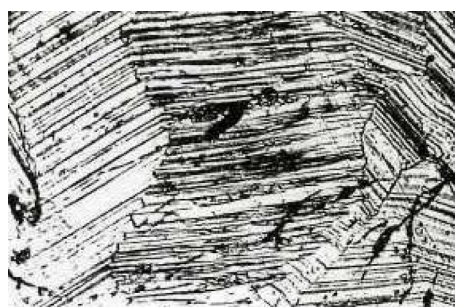


Fig. 9. Cubic phase structure based on uranium dioxide in the UO₂–ZrO₂ cathode deposits × 440.

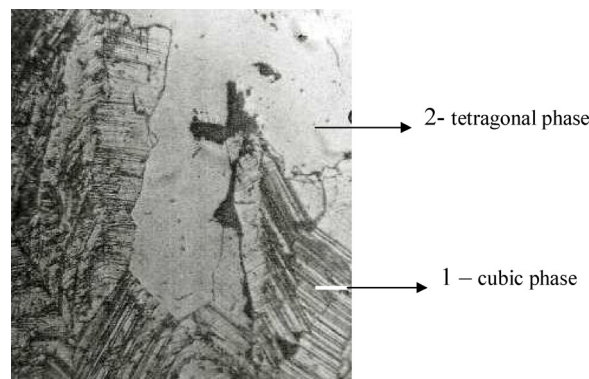


Fig. 10. Two-phase UO₂–ZrO₂ cathode deposit structure × 200.

In cathode deposits with the ZrO₂ concentration value from 6 to 36 mol. % a tetragonal phase and a cubic phase were observed (Fig. 10). The structure of the tetragonal phase was not detected. According to the UO₂–ZrO₂ system phase diagram [1,23–25] these two phases are simultaneously present in the oxide phase within the zirconium dioxide concentration from 10 to 85 mol.% and have a constant composition.

At higher ZrO₂ concentrations the cathode deposits contained three phases: cubic, tetragonal and monoclinic. They were observed on the cross section of the cathode product (Fig. 11).

Monoclinic phase was always observed in initial layers of the cathode deposit at the surface adjacent to the cathode. Two other phases (cubic and tetragonal) were observed behind the monoclinic phase and were simultaneously present in that part of the deposit. Uranium and zirconium spreading in these three phases and scanning direction of the cross section of other cathode deposit is demonstrated in Figs. 12 and 13.

Data on X-ray spectral microanalysis (Fig. 13) allowed evaluating the composition of these phases. The monoclinic phase contains 88–94 mol. % of ZrO₂, the tetragonal phase contains 74–77 mol. % of ZrO₂ and the cubic phase contains 6–8 mol. % of ZrO₂. These results are close to the phase composition in the UO₂–ZrO₂ system [1,23–25].

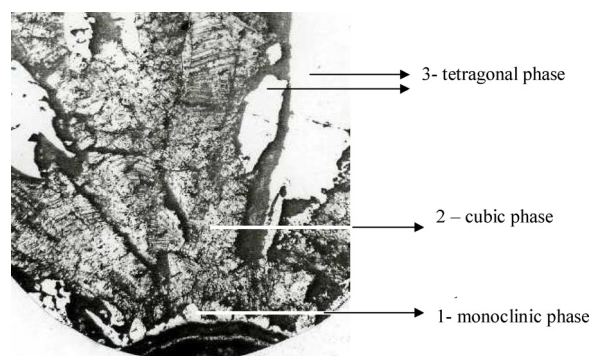


Fig. 11. Three-phase UO₂–ZrO₂ cathode deposit structure × 70.

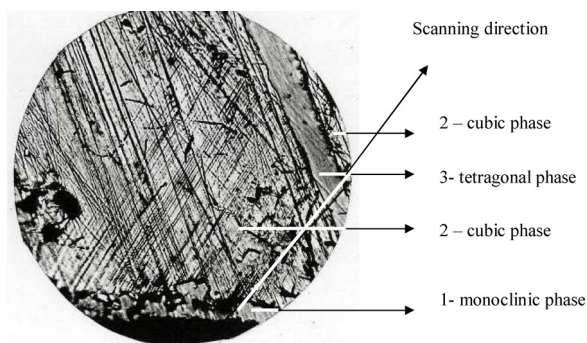


Fig. 12. Cross-section of the three-phase $\text{UO}_2\text{-ZrO}_2$ cathode deposit $\times 440$. (without treating with reagents)

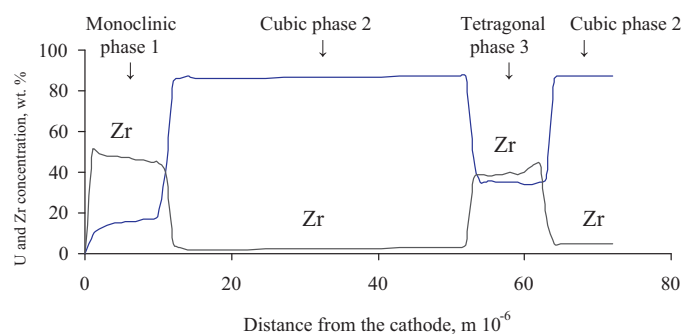


Fig. 13. Uranium and zirconium concentration in the three-phase $\text{UO}_2\text{-ZrO}_2$ cathode deposit.

Thus, qualitative and quantitative composition of cathode deposits agrees with the phase diagram of the $\text{UO}_2\text{-ZrO}_2$ system [1,23–25].

4. CONCLUSIONS

- 1 Cathode deposit formation, including the simultaneous electrolytic reduction of UO_2^{2+} ions to UO_2 and the exchange between the growing cathode deposit and the electrochemically inactive electrolyte component (ZrCl_4), was analyzed using the $\text{UO}_2\text{-ZrO}_2$ system.
- 2 The cathode $\text{UO}_2\text{-ZrO}_2$ deposits, which contained up to 98 mol. % ZrO_2 , were formed.
- 3 The influence of the ZrCl_4 concentration in the $(\text{NaCl-KCl})_{\text{equim}}\text{-UO}_2\text{Cl}_2\text{-ZrCl}_4$ melt, the initial electrolysis current density, the temperature, and the electrolysis duration on the average ZrO_2 concentration in the $\text{UO}_2\text{-ZrO}_2$ deposits was studied.
- 4 The ZrO_2 fraction in the cathode $\text{UO}_2\text{-ZrO}_2$ deposits regularly decreased as the ZrCl_4 concentration decreased and the current density and electrolysis duration increased.
- 5 The influence of electrolyte temperature on the average composition of the cathode $\text{UO}_2\text{-ZrO}_2$ deposits was insignificant.
- 6 The phase composition of the $\text{UO}_2\text{-ZrO}_2$ cathode deposits was detected. When the ZrO_2 concentration in the cathode deposits was lower than 6 mol %, only the UO_2 -based cubic phase was observed; as the ZrO_2 concentration increase to 36 mol % the ZrO_2 -based tetragonal phase was detected along with the cubic one; at higher ZrO_2 concentrations all three phases were found in the cathode deposits: UO_2 -based cubic phase, ZrO_2 -based tetragonal phase and ZrO_2 -based monoclinic phase.

7 The experimental results attributed to changes in rates of the simultaneous electrolytic reduction of UO_2^{2+} to UO_2 and exchange between UO_2 and Zr^{4+} ions, which were present in the molten electrolyte.

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