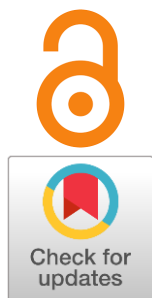


Mechanism of interaction between zirconium dioxide and fluoride melts

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In this work, the mechanism of interaction between zirconium dioxide and fluoride melts was studied. Dissolution rates and maximum permissible oxide contents in the KF-AlF₃ and NaF-AlF₃ melts were determined under natural convection conditions at a temperature of 750 °C. The results of solubility measurement show that the limiting content of ZrO₂ in the KF-AlF₃ melt ([KF]/[AlF₃] = 1.3) is 0.69 ± 0.10 mol. %, and in the NaF-AlF₃ melt ([NaF]/[AlF₃] = 1.3) at 800 °C it is 0.54 ± 0.04 mol. %. The calculated dissolution rate of zirconium oxide under these conditions in melts based on potassium fluoride and sodium fluoride is 0.022 mol/min and 0.017 mol/min, respectively. The influence of the cationic composition of the medium and the concentrations of additives on the liquidus temperatures of the melts was studied. It has been established that the increase in liquidus and solidus temperatures is facilitated by the addition of zirconium and aluminium oxides, as well as by the replacement of potassium fluoride with sodium fluoride while maintaining the molar ratio of the replaced cations. Analysis of thermal effects by differential scanning calorimetry (DSC) shows that, regardless of the molar ratio of the components, the onset of the thermal effect in melts based on potassium fluoride occurs at a temperature of 542 °C and in the systems with sodium fluoride additives at a temperature of 597 °C. Presumably, this dependence is associated with the melting of the KAIF₄ and K₂NaAlF₇ phases formed in the melts based on KF-AlF₃ and KF-NaF-AlF₃, respectively. It has been established that the melting of the KF-AlF₃ mixture is accompanied with a mass loss of up to 1.3 wt. %, which is associated with partial evaporation of KAIF₄.

keywords: zirconium, oxide, melt, fluorides, dissolution, interaction, mechanism

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1. Introduction

Zirconium and its compounds are widely used in all industrial fields, from medicine to nuclear energy. The electrolysis of molten salts is a promising method for producing both metallic zirconium and zirconium-based materials. Compared to aqueous electrochemistry, the main advantage of high-temperature processes is the combination of high intensity with the possibility of using water-insoluble compounds. It is preferable to maintain the required content of zirconium ions by periodical loading of zirconium-containing components into the melt. A necessary condition for the practical implementation of this method is the possibility to dissolve the target compounds in a salt flux with the formation of electroactive ions. From this viewpoint, zirconium oxide is the most suitable metal-containing

component, due to its low cost, availability, i.e., it can be produced in the desired amounts. On the other hand, the melts based on fluorides of alkali and alkaline earth metals are promising media for the dissolution of oxides [1–4].

Since the kinetics of the interaction between zirconium oxide and the electrolyte determine the kinetics of the electrolytic production of zirconium and materials based on it, and since the information on these parameters is limited in the scientific and technical literature, the study of the mechanism of interaction between zirconium oxide and fluoride melts is highly relevant.

2. Experimental

To obtain more accurate measurement results, we used melts that were additionally purified from foreign impurities and moisture according to standardized methods [1]. All electrolytes were prepared by mixing the following initial salts: commercial chemically pure

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$\text{KF} \times \text{HF}$, NaF , AlF_3 (Vekton JSC, Russia) [5, 6]. Aluminum fluoride was mixed with ammonium fluoride and heated to $450\text{ }^\circ\text{C}$, and exposed at this temperature for 4 hours until NH_4F was completely decomposed. When heated, NH_4F decomposes into ammonia and hydrogen fluoride that reacts with oxides. After purification, the composition of the resulting mixture was adjusted to the required molar ratio $[\text{KF}]/[\text{AlF}_3]$ by adding KF obtained by thermal decomposition of $\text{KF} \times \text{HF}$ that was heated for 12 hours at $900\text{ }^\circ\text{C}$. The NaF-AlF_3 melt was obtained by similar mixing and melting of the mixture in given proportions in the presence of NH_4F for 12 hours. KF-NaF-AlF_3 melts were obtained by mixing pre-prepared KF-AlF_3 and NaF-AlF_3 melts. To remove the remaining impurities and oxides, the melts were subjected to the purifying potentiostatic electrolysis at a graphite cathode potential of -1.1 V relative to the CO/CO_2 electrode [7] for 2 hours. Commercial chemically pure zirconium oxide (Vekton JSC, Russia) and aluminium oxide (Achinsk Alumina Refinery JSC, Russia) were loaded into the reactor immediately before measurements.

The liquidus temperatures of the melts and the solubility of ZrO_2 were measured in the cell shown in Figure 1.

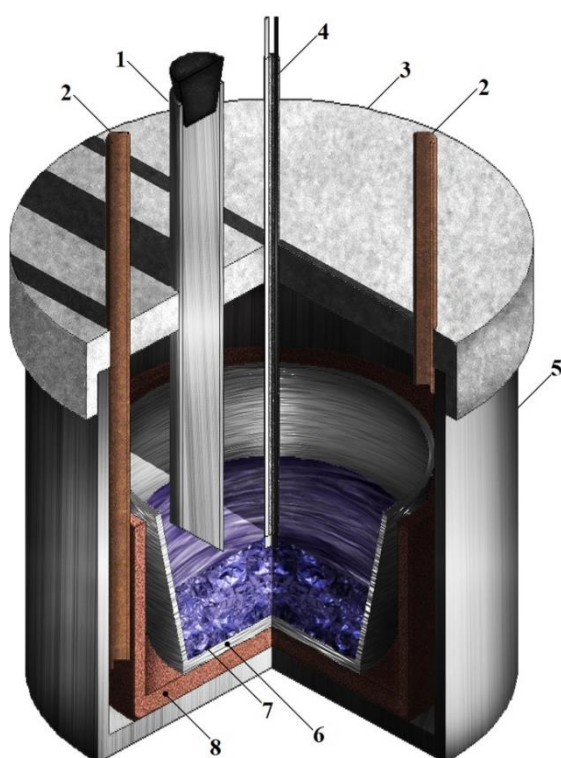


Figure 1 Diagram of the experimental cell for measuring the liquidus temperatures of the studied melts with ZrO_2 and Al_2O_3 additives: 1 – quartz tube; 2 – alumina tube; 3 – fluoroplastic cover; 4 – thermocouple; 5 – quartz retort; 6 – platinum crucible; 7 – melt under study; 8 – protective alumina glass.

The prepared mixture weighing 100 g was loaded into a platinum crucible (6) located in an alumina beaker (8). The cell was placed in a quartz retort (5) with a fluoroplastic lid (3). Before carrying out measurements, the retort was pre-evacuated, and during the measurements it was purged with high-purity argon. The experimental cell was heated in a resistance furnace with silicon carbide heaters. The temperature was controlled using a Varta TP-403 thermostat and a platinum-platinum-rhodium thermocouple within $\pm 2\text{ }^\circ\text{C}$. The measurements were carried out according to the method described in [8, 9]. The mixture under study was melted at a temperature of $900\text{ }^\circ\text{C}$. Then the furnace was cooled at a rate of 3 degrees/min, and the changes in melt temperature were recorded with a platinum-platinum-rhodium (Pt/Pt-Rh) thermocouple (4) immersed directly into the melt. Zirconium and aluminium oxides were loaded into the melt through a quartz tube (1) using a sluice, with excess argon pressure in a quartz retort. Through it, the samples of studied melts were taken to perform chemical analysis.

Elemental compositions were analyzed by the spectral emission method with inductively coupled plasma (ICP), using an iCAP 6300 Duo optical emission spectrometer (Thermo Scientific, USA). The phase composition of the melts was analyzed by the X-ray diffraction analysis (XRD analysis) using a D/MAX-2200VL/PC X-ray diffractometer (Rigaku, Japan).

To obtain more accurate data on thermal effects, the studied melts were analyzed by differential scanning calorimetry (DSC). To determine the stability of the melts during the melting process, the resulting electrolytes were analyzed by the thermogravimetric analysis (TG) using an STA 449 F1 Jupiter thermal analyzer with a QMS 403C Aëolos mass spectrometer (Netzsch, Germany). To determine the solubility and dissolution rate of oxides, the electrolyte under study was melted and kept at a given temperature in a platinum crucible, and the dissolution kinetics was studied by the melt. To do this, the required amount of oxide was loaded into the melt and samples were taken at certain time intervals. To eliminate errors in measurements, powders from the same batch were used; the particles size was $20\text{--}50\text{ }\mu\text{m}$ and the specific surface area was $9.68 \pm 0.09\text{ m}^2/\text{g}$.

3. Results and discussions

Figures 2 and 3 show the results of measuring the solubility and dissolution rate of zirconium oxide in the studied melts [10, 11]. According to the results of chemical analysis of samples taken after keeping the oxide in the

melt for 60, 120 minutes, the zirconium content in them corresponded to the amount of zirconium in the loaded oxide within the error. When 1.5 wt. % ZrO_2 was added to the melt, incomplete dissolution of the sample was observed in the $KF-AlF_3$, and $NaF-AlF_3$ based melts after 120 minutes according to the spectral analysis. According to the results obtained, the maximum zirconium content in the $KF-AlF_3$ melt ($[KF]/[AlF_3] = 1.3$) at 750 °C was 0.69 ± 0.10 mol. %, and in the $NaF-AlF_3$ melt ($[NaF]/[AlF_3] = 1.3$) at 800 °C it was 0.54 ± 0.04 mol. %.

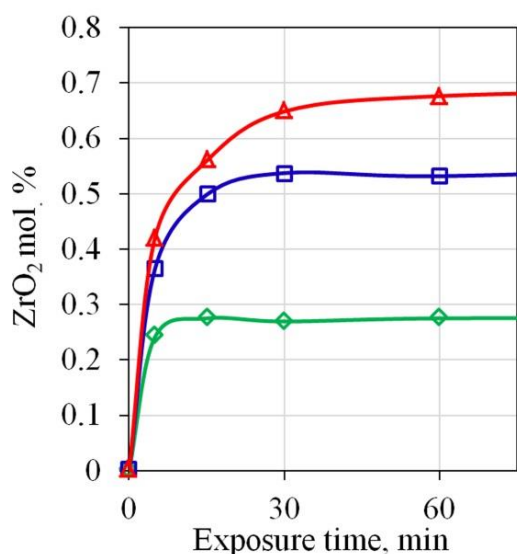


Figure 2 ZrO_2 content in the $KF-AlF_3$ melt ($[KF]/[AlF_3] = 1.3$) at 750 °C after adding ZrO_2 in the amount of wt. % (mol. %): \diamond - 0.5 (0.28), \square - 1.0 (0.56), Δ - 1.5 (0.84).

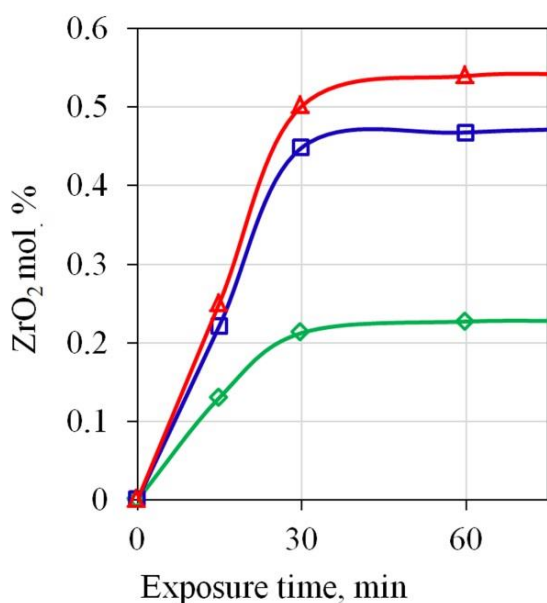


Figure 3 ZrO_2 content in the $NaF-AlF_3$ melt ($[NaF]/[AlF_3] = 1.3$) at 750 °C after adding ZrO_2 in the amount of wt. % (mol. %): \diamond - 0.5 (0.28), \square - 1.0 (0.56), Δ - 1.5 (0.84).

Based on the initial linear sections of the obtained dependences, the dissolution rate of zirconium oxide was calculated; it was 0.022 mol/min for the $KF-AlF_3$ -based melt at 750 °C and 0.017 mol/min for a $NaF-AlF_3$ melt at 800 °C. Despite the higher temperature, the dissolution rate of ZrO_2 in a melt based on sodium fluoride is lower than in a melt based on potassium fluoride, consistent with known data on the solubility of other oxides in these melts [12]. Based on the data obtained, we can conclude that, from the viewpoint of the dissolution rate of ZrO_2 , it is preferable to use melts based on the $KF-AlF_3$ system.

Since melts containing AlF_3 interact with the loaded zirconium oxide to form complex compounds and aluminum oxide [11–13], the question of studying the joint solubility of ZrO_2 and Al_2O_3 in the studied media is relevant. As a result of the research, it was found that the introduction of sodium fluoride into the $KF-AlF_3$ melt reduces its volatility, and therefore, for further research, a $KF-AlF_3$ -based melt with the addition of 10 wt. % sodium fluoride was selected.

The dependences of the liquidus temperatures of the melts ($[KF] + [NaF] / [AlF_3] = 1.3$) on the content of zirconium and aluminum oxide obtained by the isothermal saturation method are shown in Figure 4. The addition of zirconium and aluminum oxides leads to an additive effect of the increase in liquidus temperature by almost 80 °C. Based on the results obtained, we can conclude that, under other constant conditions, the presence of oxides in the melt will lead to a decrease in the solubility of other oxide additives, which is

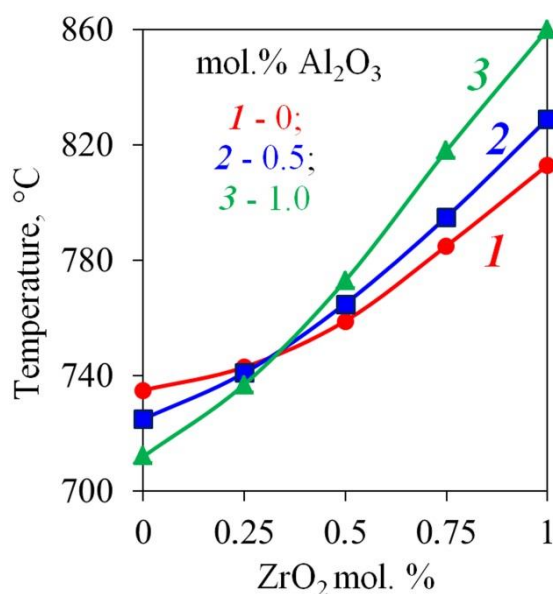


Figure 4 Liquidus temperatures of $KF-NaF-AlF_3$ melts depending on the content of ZrO_2 and Al_2O_3 ($[KF] + [NaF] / [AlF_3] = 1.3$).

presumably due to the saturation of the melt with the oxygen ions.

For a more detailed study of the effect of oxide additions to fluoride melts, the effect of oxide additions on thermal effects in the KF-AlF₃ and KF-NaF-AlF₃ systems was studied using the differential scanning calorimetry (DSC). The obtained data are shown in Figure 5 and Table 1. Regardless of the [KF]/[AlF₃] ratio, the onset of the thermal effect in the melt occurs at a temperature of 542 °C, which is presumably associated with the melting of KAlF₄. In systems with sodium fluoride additives, the thermal effect is observed at a temperature of 597 °C, which, according to literature data, is associated with the melting of K₂NaAl₃F₁₂ [14–17]. It was also found that during heating to a temperature of 800 °C there was no noticeable loss in the mass of the samples (Figure 6). With further heating, a mass loss of up to 1.3 % was noted. This may be associated with the partial evaporation of KAlF₄.

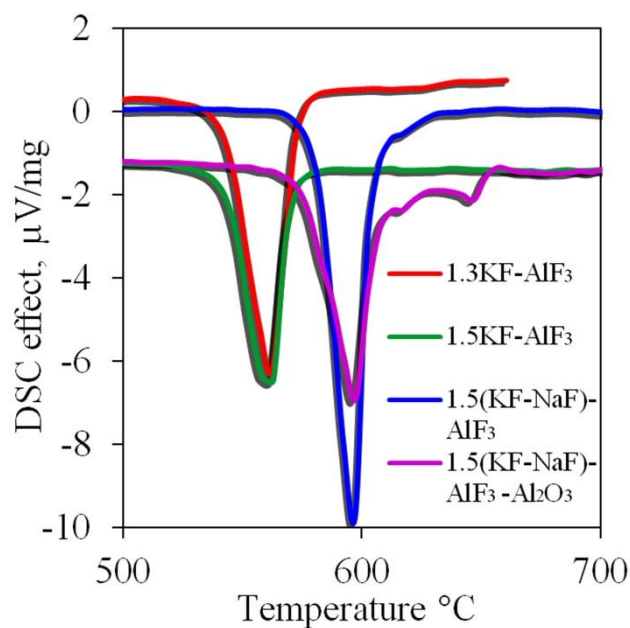


Figure 5 Thermal effects in the mixtures of KF-AlF₃, KF-NaF-AlF₃ and KF-NaF-AlF₃-Al₂O₃ with the addition of 1.0 mol. % ZrO₂ when heated to 800 °C.

Table 1 – DSC data in the studied oxide-fluoride mixtures.

Melt composition	[(KF) + [NaF)]/[AlF ₃]	Solidus temperature, °C	Peak temperature, °C
KF-AlF ₃ -ZrO ₂	1.3	542	563
KF-AlF ₃ -ZrO ₂	1.5	545	597
KF-NaF-AlF ₃ -ZrO ₂	1.3	580	562
KF-NaF-AlF ₃ -Al ₂ O ₃ -ZrO ₂	1.3	573	597, 647

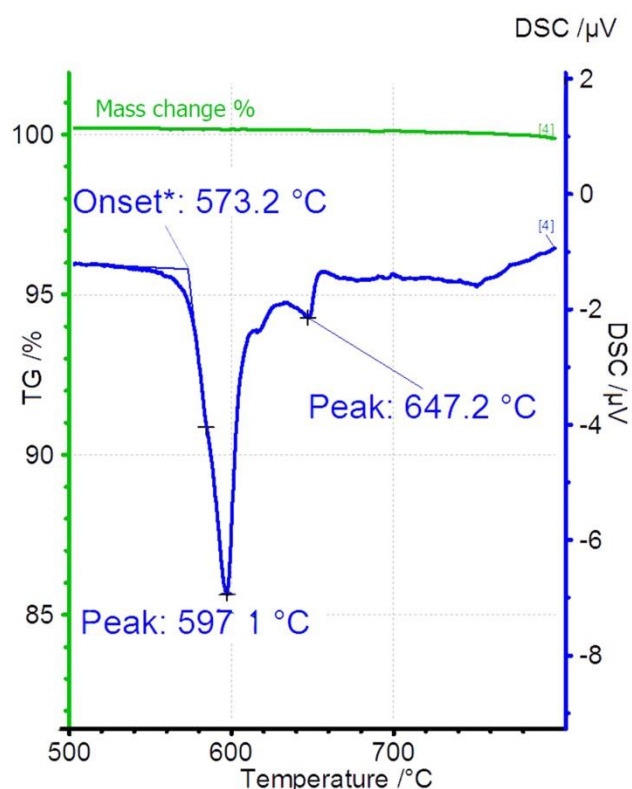


Figure 6 Thermal effects and change in the mass of the KF-NaF-AlF₃-Al₂O₃ (1.0 mol. % ZrO₂) mixture during its heating to 800 °C.

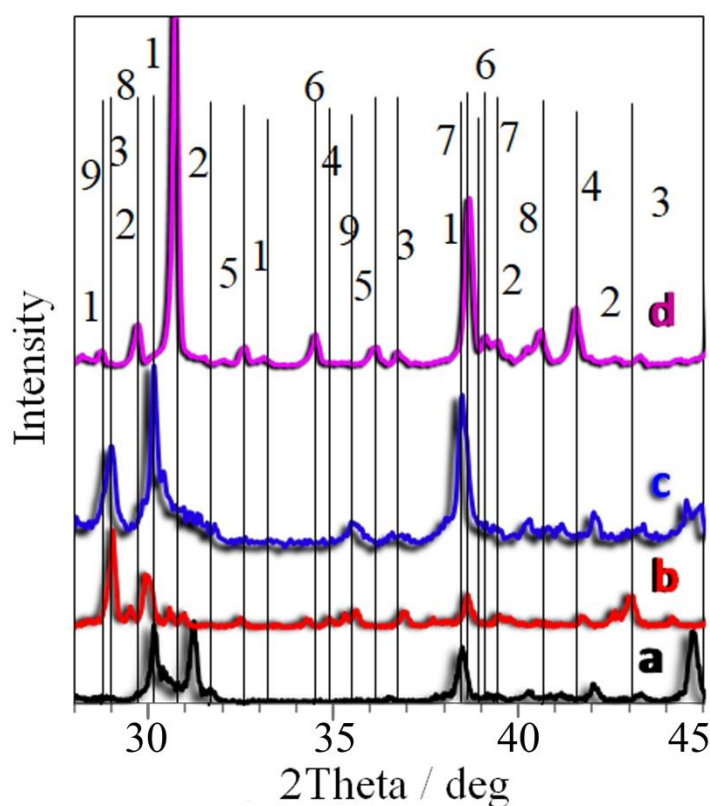
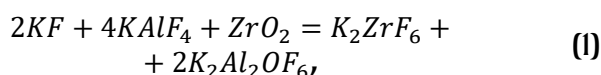
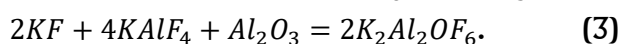
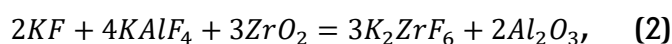


Figure 7 Diffraction patterns of the studied oxide-fluoride mixtures after ZrO₂ dissolution.

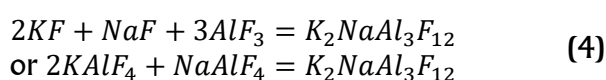
To clarify the mechanism of interaction between zirconium and aluminium oxides and fluoride melts, the effect of oxide additives on the phase composition of the resulting melts was studied. Figure 7 shows the X-ray phase analysis data according to which the KAlF_4 , K_2ZrF_6 , ZrO_2 and Al_2O_3 phases were found in the $\text{KF-AlF}_3\text{-ZrO}_2$ systems (Figure 7a). The melts with additions of sodium fluoride also contain K_2NaAlF_6 and $\text{K}_2\text{NaAl}_3\text{F}_{12}$ phases (Figures 7b and c), which confirms the assumptions obtained previously by DSC. The data obtained indicate that the interaction between zirconium dioxide and fluoride melts based on the KF-AlF_3 and KF-NaF-AlF_3 systems proceeds with the formation of Al_2O_3 and potassium hexafluorozirconate (Figures 7a, b), while it is known [12–18] that the dissolution of Al_2O_3 in the KF-AlF_3 melts occurs with the formation of complex $\text{Al}_2\text{OF}_6^{2-}$ anions. In this case, the dissolution of ZrO_2 in the melts based on the KF-AlF_3 system can be represented by the total Reaction (1):



which represents two series-parallel Reactions (2) and (3):



When sodium fluoride is added to the KF-AlF_3 melt, the $\text{K}_2\text{NaAl}_3\text{F}_{12}$ compound is formed according to Reactions (4), which is confirmed by the results of the X-ray diffraction analysis (Figure 7b):



An increase in the liquidus temperatures of melts based on the KF-AlF_3 systems by 50–100 °C with the addition of ZrO_2 is explained by the complication of both the composition and the structure of the multicomponent $\text{KF-KAlF}_4\text{-K}_2\text{ZrF}_6\text{-Al}_2\text{O}_3$ melt, [12–18], which is consistent with previously obtained experimental and literature data. The proposed mechanism of zirconium oxide dissolution in fluoride melts is confirmed by the consistency of experimental data obtained by independent methods (thermal analysis, DSC, thermogravimetry, X-ray phase analysis) as well as by scientific and technical literature data including known ideas on the behavior of oxides in halide melts. All compounds and their corresponding peaks in the diffraction patterns are given in Table 2.

Table 2 – Compounds detected in diffraction patterns.

Melt composition	Number on the graphic	Phase composition
$\text{KF-AlF}_3\text{-ZrO}_2$	1	KAlF_4 ;
	2	K_2ZrF_6 ;
	3	ZrO_2 ;
	4	Al_2O_3
$\text{NaF-AlF}_3\text{-ZrO}_2$	5	$\text{Na}_6\text{Al}_3\text{F}_{14}$;
	6	Na_3AlF_6 ;
	7	ZrF_4
$\text{KF-NaF-AlF}_3\text{-ZrO}_2$	1–7	all of the above
	8	K_2NaAlF_6 ;
	9	$\text{K}_2\text{NaAl}_3\text{F}_{12}$
$\text{KF-NaF-AlF}_3\text{-Al}_2\text{O}_3\text{-ZrO}_2$	1–9	all of the above

4. Conclusions

The mechanism of interaction between zirconium oxide and alkali metal fluorides was studied in this work. It has been established that in the MeF-AlF_3 system (where $\text{Me} = \text{K}, \text{Na}$), when potassium fluoride is replaced by sodium fluoride, the solubility of zirconium oxide reduces slightly. Additions of zirconium and aluminum oxides increase the liquidus temperatures of the melts, which is associated with the complication of the mixture composition and the formation of a number of intermediate compounds. A study of thermal effects obtained by differential scanning calorimetry shows that, regardless of the $[\text{KF}]/[\text{AlF}_3]$ ratio, the onset of the thermal effect in the KF-AlF_3 melts occurs at a temperature of 542 °C and with the addition of sodium fluoride it occurs at a temperature of 597 °C, which is associated with melting of the KAlF_4 and $\text{K}_2\text{NaAl}_3\text{F}_{12}$ phases, respectively. Analysis of the obtained diffraction patterns of the studied oxide-fluoride mixtures elucidates that the dissolution of zirconium oxide in fluoride melts proceeds with the formation of Al_2O_3 and potassium hexafluorozirconate; the addition of sodium cations leads to the additional formation of a series of more complex compounds.

Supplementary materials

No supplementary materials are available.

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None.

Author contributions

Aleksandr Filatov: Conceptualization; Investigation; Methodology; Data curation; Writing – Original draft; Writing – Review & Editing; Formal Analysis; Visualization.

Conflict of interest

The authors declare no conflict of interest.

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