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# 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-AlF$_3$ and NaF-AlF$_3$ melts were determined under natural convection conditions at a temperature of 750 °C. The results of solubility measurement show that the limiting content of $ZrO_2$ in the KF-AlF$_3$ melt ($[KF]/[AlF_3] = 1.3$) is $0.69 \pm 0.10$ mol. %, and in the NaF-AlF$_3$ melt ($[NaF]/[AlF3] = 1.3$) at 800 °C it is $0.54 \pm 0.04$ 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 $KAlF_4$ and $K_2NaAl_3F_{12}$ phases formed in the melts based on KF-AlF$_3$ and KF-NaF-AlF$_3$, respectively. It has been established that the melting of the KF-AlF$_3$ mixture is accompanied with a mass loss of up to 1.3 wt. %, which is associated with partial evaporation of $KAlF_4$.

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

## 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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KF×HF, NaF, $AlF_3$ (Vekton JSC, Russia) [5, 6]. Aluminum fluoride was mixed with ammonium fluoride and heated to 450 °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 [KF]/[$AlF_3$] by adding KF obtained by thermal decomposition of KF×HF that was heated for 12 hours at 900 °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.

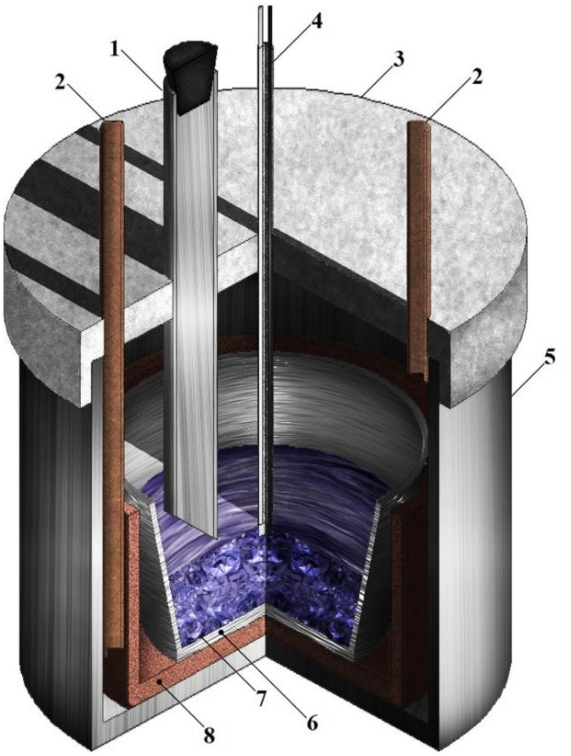

**Figure 1** Diagram of the experimental cell for measuring the liquidus temperatures of the studied melts with $ZrO_2$ and $Al_2O_3$ additives: 1 – quartz tube; 2 – alundum tube; 3 – fluoroplastic cover; 4 – thermocouple; 5 – quartz retort; 6 – platinum crucible; 7 – melt under study; 8 – protective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

The prepared mixture weighing 100 g was loaded into a platinum crucible (6) located in an alundum 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 ± 2 °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 °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 20–50 μm and the specific surface area was 9.68 ± 0.09 $m^2/g$.

## 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. %.

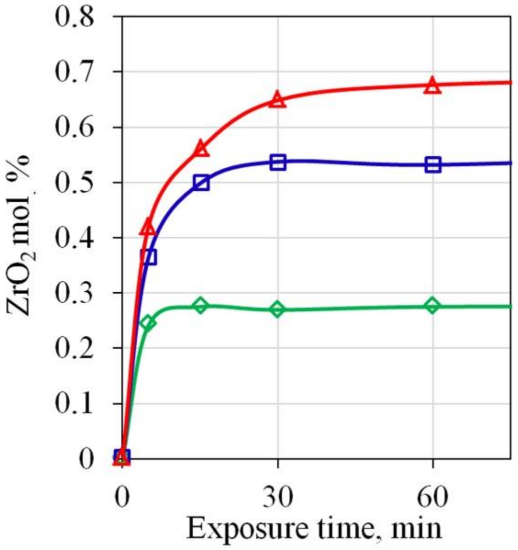

**Figure 2** $ZrO_2$ content in the KF-$AlF_3$ melt ([KF]/[$AlF_3$] = 1.3) at 750 °C after adding $ZrO_2$ in the amount of wt. % (mol. %): ◊ – 0.5 (0.28 ), □ – 1.0 (0.56), Δ – 1.5 (0.84).

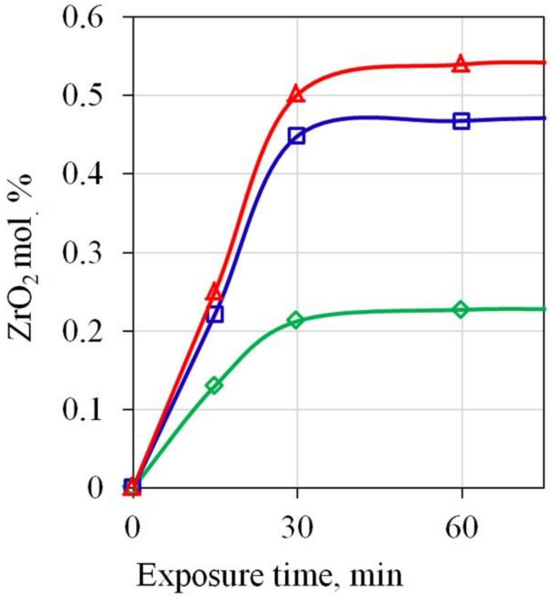

**Figure 3** $ZrO_2$ content in the NaF-$AlF_3$ melt ([NaF]/[$AlF_3$] = 1.3) at 750 °C after adding $ZrO_2$ in the amount of wt. % (mol. %): ◊ – 0.5 (0.28 ), □ – 1.0 (0.56), Δ – 1.5 (0.84).

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

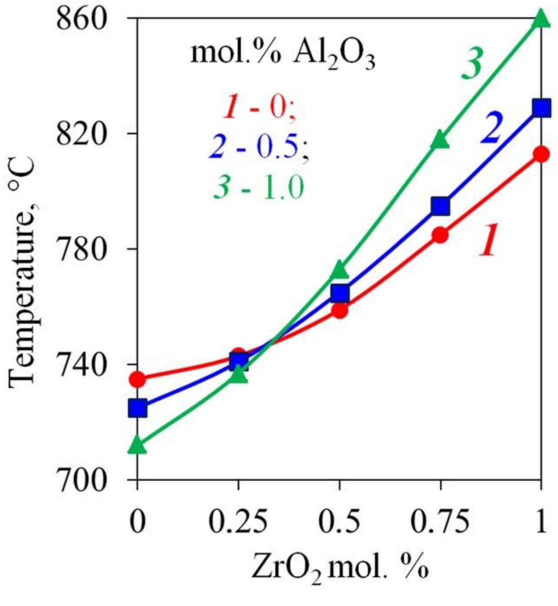

**Figure 4** Liquidus temperatures of KF-NaF-$AlF_3$ melts depending on the content of $ZrO_2$ and $Al_2O_3$ ([KF] + [NaF])/[$AlF_3$] = 1.3).

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-$AlF_3$ and KF-NaF-$AlF_3$ systems was studied using the differential scanning calorimetry (DSC). The obtained data are shown in Figure 5 and Table 1. Regardless of the [KF]/[$AlF_3$] 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 $KAlF_4$. 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 $K_2NaAl_3F_{12}$ [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 $KAlF_4$.

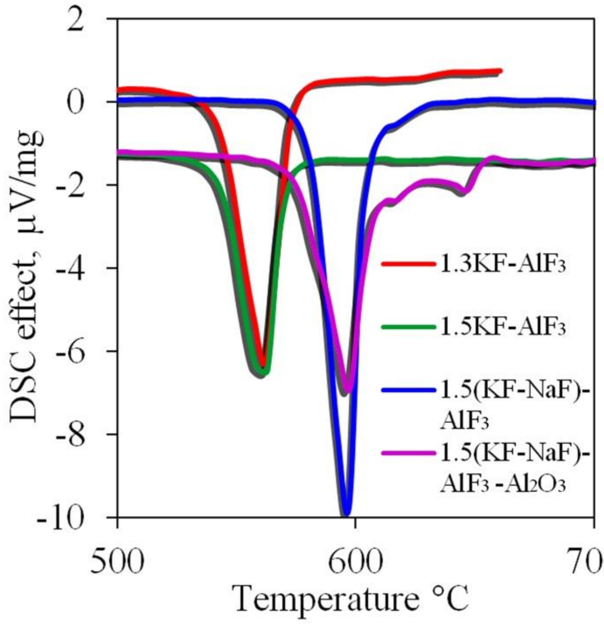

**Figure 5** Thermal effects in the mixtures of KF-$AlF_3$, KF-NaF-$AlF_3$ and KF-NaF-$AlF_3$-$Al_2O_3$ with the addition of 1.0 mol. % $ZrO_2$ when heated to 800 °C.

**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-$AlF_3$- -$Al_2O_3$-$ZrO_2$ | 1.3 | 573 | 597, 647 |

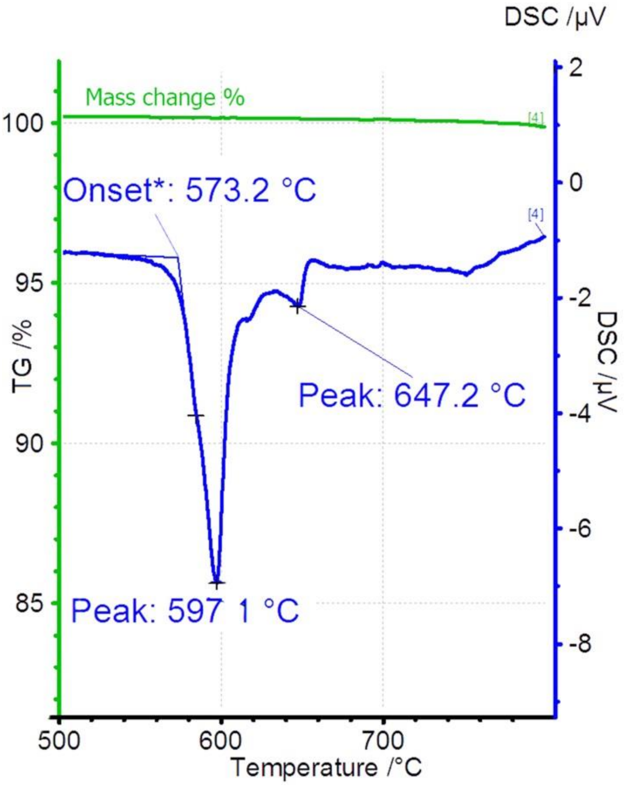

**Figure 6** Thermal effects and change in the mass of the KF-NaF-$AlF_3$-$Al_2O_3$ (1.0 mol. % $ZrO_2$) mixture during its heating to 800 °C.

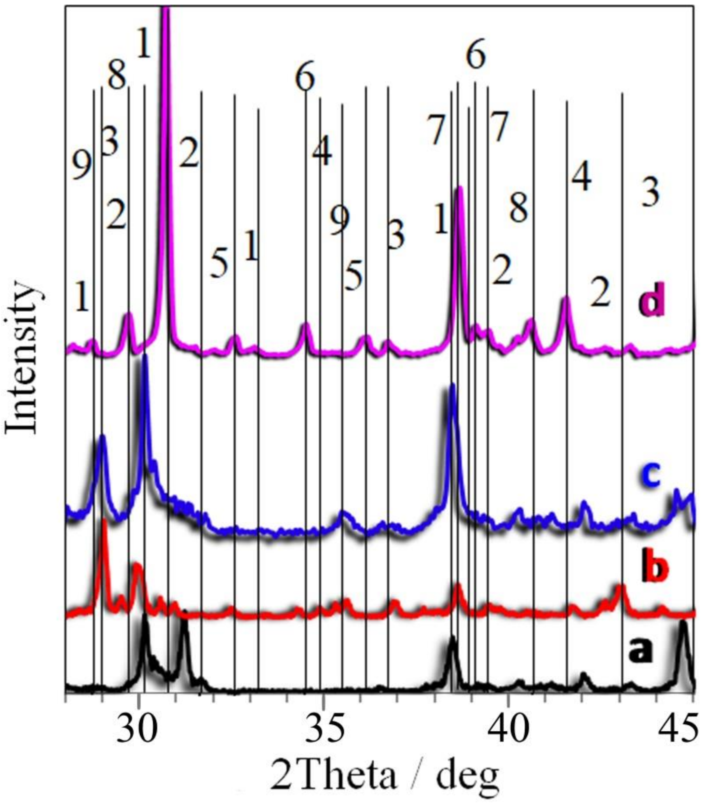

**Figure 7** Diffraction patterns of the studied oxide-fluoride mixtures after $ZrO_2$ dissolution.

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 $KF$-$AlF_3$-$ZrO_2$ systems (Figure 7a). The melts with additions of sodium fluoride also contain $K_2NaAlF_6$ and $K_2NaAl_3F_{12}$ 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 $Al_2OF_6^{2-}$ 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):

$$\begin{aligned}2KF + 4KAlF_4 + ZrO_2 = K_2ZrF_6 + \\ + 2K_2Al_2OF_6,\end{aligned} \tag{1}$$

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

$$2KF + 4KAlF_4 + 3ZrO_2 = 3K_2ZrF_6 + 2Al_2O_3, \tag{2}$$

$$2KF + 4KAlF_4 + Al_2O_3 = 2K_2Al_2OF_6. \tag{3}$$

When sodium fluoride is added to the $KF$-$AlF_3$ melt, the $K_2NaAl_3F_{12}$ compound is formed according to Reactions (4), which is confirmed by the results of the X-ray diffraction analysis (Figure 7b):

$$\begin{aligned}2KF + NaF + 3AlF_3 = K_2NaAl_3F_{12} \\ \text{or } 2KAlF_4 + NaAlF_4 = K_2NaAl_3F_{12}\end{aligned} \tag{4}$$

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 $KF$-$KAlF_4$-$K_2ZrF_6$-$Al_2O_3$ 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 |
|---|---|---|
| $KF$-$AlF_3$-$ZrO_2$ | 1 | $KAlF_4$; |
| | 2 | $K_2ZrF_6$; |
| | 3 | $ZrO_2$; |
| | 4 | $Al_2O_3$ |
| $NaF$-$AlF_3$-$ZrO_2$ | 5 | $Na_6Al_3F_{14}$; |
| | 6 | $Na_3AlF_6$; |
| | 7 | $ZrF_4$ |
| $KF$-$NaF$-$AlF_3$-$ZrO_2$ | 1–7 | all of the above |
| | 8 | $K_2NaAlF_6$; |
| | 9 | $K_2NaAl_3F_{12}$ |
| $KF$-$NaF$-$AlF_3$-$Al_2O_3$--$ZrO_2$ | 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 *Me*F-$AlF_3$ system (where *Me* = K, 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 $[KF]/[AlF_3]$ 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 $K_2NaAl_3F_{12}$ 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.

## Additional information

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## References

1. Tkacheva O, Redkin A, Kataev A, Rudenko A, et al., Novel molten salts media for production of functional materials, MATEC Web of Conferences, **67** (2016) 1–6. https://doi.org/10.1051/matecconf/20166706044

2. Pershin PS, Kataev AA, Filatov AA, Suzdaltsev AV, et al., Synthesis of Al-Zr alloys via $ZrO_2$ aluminum-thermal reduction in KF-$AlF_3$-based melts, MMTB, **48** (2017) 1962–1969. https://doi.org/10.1007/s11663-017-0976-y

3. Pershin PS, Suzdaltsev AV, Zaikov YuP, Synthesis of silumins in KF–$AlF_3$–$SiO_2$ melt, JES, **163(5)** (2016) 167–170. https://doi.org/10.1149/2.0521605jes

4. Suzdaltsev AV, Khramov AP, Zaikov YuP, Carbon electrode for electrochemical studies in cryolite-alumina melts at 700–960 °C, Russ. J Electrochem., **48** (2012) 1141–1152. https://doi.org/10.1134/S1023193512120117

5. Apisarov A, Juan B, Dedyukhin A, Galan L, et al., Reduction of the operating temperature of aluminum electrolysis: Low temperature electrolyte, Light Met. (2012) 783–786. https://doi.org/10.1002/9781118359259.ch135

6. Apisarov A, Dedyukhin A, Tinghaev P, Redkin A, et al., Liquidus Temperatures of Cryolite Melts With Low Cryolite Ratio, MMTB, **42** (2010) 236–242. https://doi.org/10.1007/s11663-010-9462-5

7. Danielik V, Hives J, Low-Melting Electrolyte for Aluminum Smelting, J. of Chem. and Eng. Data, **35(47)** (2004) 1414–1417. https://doi.org/10.1002/chin.200447013

8. Peng J, Wei Z, Di Y, Wang Y, et al., Alumina Solubility in NaF-KF-LiF-$AlF_3$-Based Low-Temperature Melts, JOM, **72** (2020) 239–246. https://doi.org/10.1007/s11837-019-03873-2

9. Kirik SD, Zaitseva YuN, Leshok DYu, Samoilo AS, et al., NaF-KF-$AlF_3$ System: Phase Transition in $K_2NaAl_3F_{12}$ Ternary Fluoride, Inorg. Chem., **54(12)** (2015) 5960–5970. https://doi.org/10.1021/acs.inorgchem.5b00772

10. Picard GS, Bouyer FC, Leroy M, Bertaud Y, et al., Structures of oxyfluoroaluminates in molten cryolite-alumina mixtures investigated by DFT-based calculations, J. Molec. Struct., **368** (1996) 67–80. https://doi.org/10.1016/S0166-1280(96)90539-4

11. Nekrasov VN, Suzdaltsev AV, Limanovskaya O, Khramov AP, et al., Theoretical and experimental study of anode process on carbon in KF-$AlF_3$-$Al_2O_3$ melts, Electrochim. Acta., **75** (2012) 296–304. https://doi.org/10.1016/j.electacta.2012.05.007

12. Filatov AA, Pershin PS, Suzdaltsev AV, Nikolaev AYu, et al., Synthesis of Al-Zr Master Alloys via the Electrolysis of KF-NaF-$AlF_3$-$ZrO_2$ Melts, JES, **165(2)** (2018) 28–34. https://doi.org/10.1149/2.0571802JES

13. Suzdaltsev AV, Filatov AA, Nikolaev AYu, Pankratov AA, et al., Extraction of Scandium and Zirconium from their oxides during the electrolysis of oxide–fluoride melts, Rus. Met. (Metally), **2018** (2018) 133–138. https://doi.org/10.1134/S0036029518020180

14. Filatov AA, Suzdaltsev AV, Nikolaev AYu, Zaikov YuP, Kinetics of electrical release of zirconium and aluminum from KF–$AlF_3$–$ZrO_2$ melts, Melts, **3** (2019) 287–304. (In Russian). https://doi.org/10.1134/S0235010619030046

15. Suzdaltsev AV, Pershin PS, Filatov AA, Nikolaev AYu, et al., Review-Synthesis of Aluminum Master Alloys in Oxide-Fluoride Melts: A Review, JES, **167(10)** (2020) 102503. https://doi.org/10.1149/1945-7111/ab9879

16. Filatov AA., Suzdaltsev AV, Zaikov YuP, Comparative analysis of modern methods for producing Al – Zr alloys, Tsvetnye Metally: Metal processing, **4** (2021) 78–86. (In Russian). https://doi.org/10.17580/tsm.2021.04.13

17. Filatov AA, Suzdaltsev AV, Zaikov YuP, Modifying Ability of an Al–Zr Master Alloy, Rus. Met. (Metally), **2021** (2021) 1036–1039. https://doi.org/10.1134/S0036029521080073

18. Filatov AA, Suzdaltsev AV, Zaikov YuP, Production of Al-Zr Master Alloy by Electrolysis of the KF-NaF-$AlF_3$-$ZrO_2$ Melt: Modifying Ability of the Master Alloy, MMTB, **52(6)** (2021) 4206–4214. https://doi.org/10.1007/s11663-021-02340-1