

INTERACTION OF RARE-EARTH FLUORIDES WITH METALS IN A MOLTEN SODIUM FLUORIDE–ZIRCONIUM FLUORIDE MIX- TURE

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The paper presents the results of investigations of the interaction of rare-earth fluorides with metallic sodium and zirconium in a molten sodium fluoride–zirconium fluoride mixture. The investigations have been carried out by differential thermal analysis (DTA), X-ray phase analysis (XPA), IR spectroscopy, and chemical analysis. It has been shown that metallic sodium and zirconium reduce rare-earth fluoride in the temperature range where the constituents of reaction mixture are in solid phase to form compounds of zirconium in lower oxidation states and rare-earth metals. The dependence of the temperature at the commencement of exchange reactions on the chemical nature of rare-earth halide has been established: increase in the melting point of rare-earth fluoride leads to a rise of initial interaction temperature. The degree of reduction of rare-earth fluorides by reducing metals depends on the ratio of the constituents of the original reaction mixture.

The research carried out in recent years showed that one of the promising methods for the destruction of radioactive wastes accumulated by operating nuclear power stations and by the production of weapon plutonium is the accelerator-driven transmutation of long-lived nuclides, and that a suitable reaction medium is molten salt compositions. According to the existing infrastructure of a nuclear power system, spent fuel is fluorinated to extract uranium [1], zirconium tetrafluoride, which is part of fuel element jackets, forming the basis of fluorination products. If sodium fluoride is added to fluorination products (ZrF_4) in a 1:1 (mol) ratio, the composition formed, $NaF-ZrF_4$, will conform to the criteria for choosing fuel mixtures for nuclear reactors and will be a good carrier of nuclear transmutation products.

In the course of the operation of such reactors, a continuous change of the fuel composition takes place, which is caused by the accumulation of actinide transmutation products and structural material corrosion products. Among them are rare-earth fluorides, isotopes and fluorides of transition, alkaline, alkaline-earth elements, etc [1-3]. Most of the isotopes formed have a large thermal neutron capture cross-section, which influences the neutron-energy balance of the reactor. Besides, fission products influence the corrosion resistance of structural materials towards molten-salt fuel composition.

Whereas the nuclear transmutations that are possible to date are exhaustively studied in terms of theoretical physics, the chemistry of molten salt blanket is at the initial stage of investigation. There is no information on the general laws governing chemical interaction in fuel composition, on the effect of nuclear and chemical transformations on structural materials, efficient methods for the adjustment of the composition of fuel mixtures, their utilization, and subsequent storage.

In view of this, the investigation of chemical processes occurring in melts, which form the basis of fuel

mixtures in reactors-transmuters, is topical and is of not only scientific, but also practical interest.

This paper presents results of a study of the interactions that take place between nuclear transmutation products (simulative objects: La, Pr, Nd, Gd, Dy, Yb fluorides) and the metals that are part of the fuel element jacket, fuel mixture, and structural materials.

The investigations have been carried out by differential thermal analysis (DTA), X-ray phase analysis (XPA), chemical analysis, and IR spectroscopy. A thermodynamic evaluation of the interaction of the components of a number of systems has been performed.

EXPERIMENTAL

The DTA was made on a Q-1500 derivatograph in corundum (or alundum) crucibles for DTG investigations under dry argon since the reducing metals (Zr, Na) and rare-earth fluorides are oxidized by atmospheric oxygen [4, 5]. The heating rate of the samples under investigation was 5-10 deg/min. Aluminum oxide was used as a standard. For a more reliable protection of samples from air oxidation, they were coated with a molten $NaPO_3-V_2O_5$ mixture. According to the results of Ref [6], the presence of a protective coating of the composition (wt %) $NaPO_3$ (75)– V_2O_5 (25) does not interfere in the identification of thermoeffects which are observed between the constituents of reaction mixtures; moreover, this coating has good protective properties in thermographic investigations.

The XPA was made on a DRON-UM diffractometer with $CuK\alpha$ radiation by the powder method. The IR spectra were recorded in a frequency range of 3800... 200 cm^{-1} by means of a Specord-80M device on pelleted samples with potassium bromide. The concentration of the metals in a lead-sodium alloy was determined by a procedure described earlier [7].

Analytically pure and extra pure reagents and sublimed zirconium tetrafluoride of monoclinic system, which was obtained by dehydration and simultaneous fluorination of $ZrF_4 \cdot xHOH$ were used for the investigations [8].

The interaction between rare-earth fluorides and reducing metals was investigated in a previously prepared NaF (51 mol %)- ZrF_4 (49 mol %) mixture. The rare-earth fluoride content of this mixture was varied from 4 to 20 wt %; the ratio $Zr:MF_3$ (mol %)($M=La, Yb$) was varied from 10:1 to 4:1, and the ratio $Na:LaF_3$ was varied from 1:1 to 1:3. The samples were prepared by procedures described earlier [7, 9].

The heating curves for a NaF (51 mol %)- ZrF_4 (49 mol %) mixture exhibit only one thermoeffect at $(525 \pm 5)^\circ C$, which is characteristic of the melting of a eutectic mixture in the NaF- ZrF_4 system and is in satisfactory agreement with literature data (Fig. 1) [10].

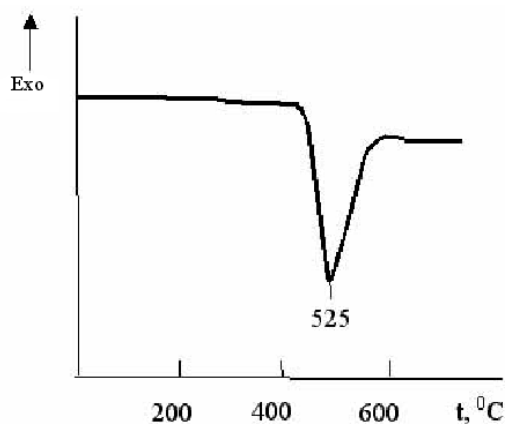


Fig. 1 Heating curve for the solvent melt NaF (51 mol %)- ZrF_4 (49 mol %)

It should be noted that alloys of the system NaF- ZrF_4 are characterized by supercooling. Indeed the cooling curves for a NaF (51 mol %)- ZrF_4 (49 mol %) mixture exhibit an effect of solidification of sodium fluoride-zirconium fluoride melt at $490^\circ C$ (Fig. 2).

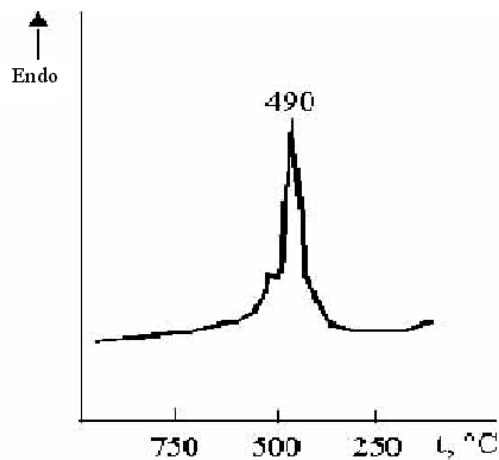


Fig. 2. Cooling curve for the solvent melt NaF (51 mol %)- ZrF_4 (49 mol %)

This phenomenon may be accounted for by the formation of thermodynamically unstable phases and their disordering. The results obtained agree with the data presented in Ref [11], where it was shown that in the NaF- ZrF_4 system at a zirconium tetrafluoride concentration of 40...60 mol %, the heating and cooling curves exhibit only one thermoeffect, independent of interaction time and temperature, the melting temperature being higher than the crystallization temperature. The compounds that are formed by interaction have close melting points and show polymorphous transformations at 160 and $440^\circ C$.

A compound of the composition $7NaF \cdot 6ZrF_4$ has been identified by an XPA (Fig. 3).

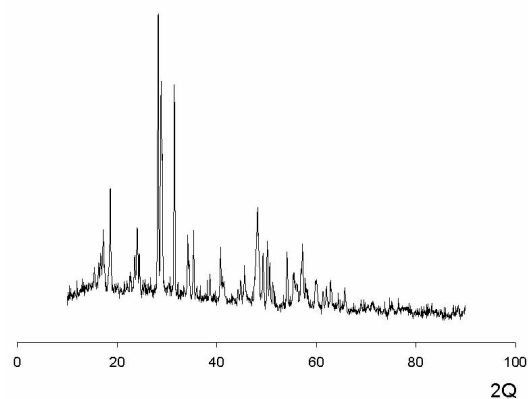


Fig. 3 Diffractogram of the NaF (51 mol %)- ZrF_4 (49 mol %) mixture

The results of the XPA of a NaF (51 mol %)- ZrF_4 (49 mol %) mixture show that a fraction is formed at the top of the melt; the fraction shows a texture, due to long soaking, which is manifested in diffractograms by a group of strong reflections from crystallographic plane with $d = 0.5077$ nm. At the bottom of the melt is a fraction, whose basis is formed by a phase with fcc lattice ($a_0 = 0.543$ nm.).

When sodium was used as a reductant, a lead-sodium melt, synthesized by the electrochemical method, was used to avoid strong interaction between rare-earth fluorides and metallic sodium, which may give rise to difficulties in the interpretation of DTG diagrams. The concentration of the metals in the alloy synthesized was determined by a procedure described earlier [7].

The NaF- ZrF_4 - LnF_3 -M systems, where $M = Zr, Na$, were investigated on samples of 1.5...3.5 g mass. Pounded mixtures were poured into a glassy carbon crucible, which was placed in a hermetically sealed metallic reactor (Fig. 4). The samples were first subjected to vacuum degassing at 200 and $300^\circ C$ and then heated under dry oxygen-free argon. The temperature in investigations did not exceed 600... $650^\circ C$.

The rare-earth metal concentration in the salt phase after the occurrence of exchange reaction was determined by complexometric titration in the presence of eriochrome black T and by gravimetric method by precipitating the rare-earth metal with oxalic acid [12]. The fluoride ion content of the reaction mixture was determined by means of a fluoride-selective electrode [13],

and sodium was determined by flame photometry. It should be noted that the presence of zirconium and lead interferes in the determination of the degree of reduction of rare-earth fluorides in the systems under investigation, therefore these metals were extracted from the samples under analysis by procedures described earlier [7, 9].

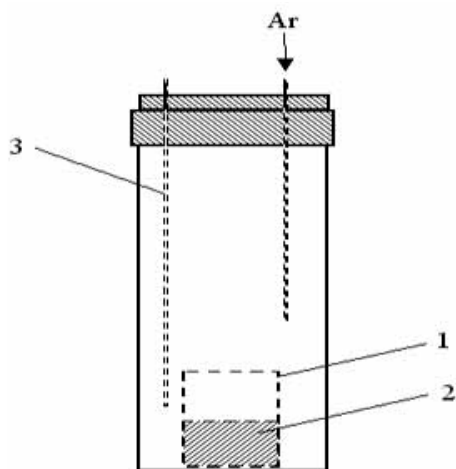
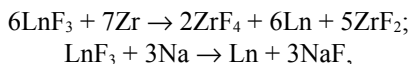


Fig. 4. Principal scheme of a reactor for the investigation of the reduction of rare-earth fluorides by reducing metals: (1) crucible, (2) sample under investigation, (3) Pt-Rh thermoconple

RESULTS AND DISCUSSION

A characteristic of the interaction between rare-earth fluorides and reducing metals is free Gibbs energy (ΔG). The exchange reaction between the constituents of the mixtures under investigation may be schematically represented as follows:



where Ln is rare-earth element. The calculations that have been made on the basis of the data obtained in Ref [14] give ground to consider the interaction between rare-earth fluorides and reducing metals to be possible on the whole since a noticeable decrease in the ΔG value is observed.

Investigation of the NaF-ZrF₄-LnF₃-Zr system. The reduction of lanthanum and ytterbium fluorides by metallic zirconium in a molten sodium fluoride-zirconium fluoride mixture takes place in a temperature range of 440...580°C, the rate of the exchange reaction depending on the fineness of reducing metal and being the higher, the higher its fineness. The differential heating curves exhibit a number of thermoeffects: endotherms of the melting of NaPO₃-V₂O₅ mixture (365 ± 5°C) and the solvent melt NaF-ZrF₄ (520 ± 5°C); an exotherm with an initial interaction temperature of 440-460°C, whose maximum is overlapped by the endotherm of the melting of a eutectic sodium fluoride-zirconium fluoride mixture. These exotherms and the thermoeffects at (460 ± 5)°C and (490 ± 5)°C may be assigned to exchange reactions between metallic zirconium and rare-earth flu-

oride and zirconium tetrafluoride with the formation of compounds of zirconium in lower-oxidation states and rare-earth metal. Since the trend of the DTA and TG curves for the samples under investigation is practically the same, a typical DTA curve for the NaF-ZrF₄-LaF₃-Zr system is shown in Fig. 5 as an example.

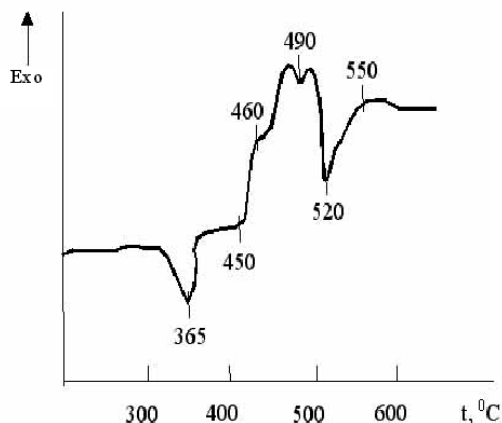


Fig. 5. Heating curve for a sample of the system NaF-ZrF₄-LaF₃-Zr containing 10 wt.% LaF₃

The results of an XPA of interaction products showed that zirconium (IV) and (II) compounds: Na₂ZrF₆, Na₇Zr₆F₃₁, Na₅Zr₂F₁₃, ZrF₂; complicated compounds comprising rare-earth fluorides and sodium fluoride, and reduced lanthanides are present in the samples under investigation. The unit cell parameters have been calculated for the identified compounds by means of a computer program; they are in satisfactory agreement with those given in publications. It should be noted that the parameters of the compound ZrF₂, which crystallizes in orthorhombic system with a = 0.40425 nm, b = 0.49537 nm, c = 0.65801 nm, have some deviations from literature data (a = 0.409 nm, b = 0.491 nm, c = 0.656 nm), which may be due to the different stoichiometry of this compound (Table 1) [15, 16].

A fragment of diffractogram of the interaction products of the system NaF-ZrF₄-Zr

Experimental data		Literature data	
Sample		ZrF ₂	
d Å°	I/I ₀ , %	d Å°	I/I ₀ , %
4,077	59	4.065	60
3,453	20	3.448	30
3,285	28	3.279	60
2,942	14	2.933	10
2,779	67	2.762	100
1,918	57	1.923	10
1,731	15	1.739	10
1,654	24	1.664	60
1,545	20	1.541	30
1,479	20	1.484	60
1,378	32	1.377	60
1,319	19	1.316	30

IR spectroscopic investigations of NaF-ZrF₄ samples showed the absorption bands to correspond to the vibra-

tion frequency range of $(ZrF_4)_n$ groupings ($n = 6 \dots 8$). The most intense absorption band at $490\text{--}500\text{ cm}^{-1}$ relates to Zr-F bridge bond stretching vibrations and that at $580\text{--}590\text{ cm}^{-1}$ to Zr-F nonbridge bond stretching vibrations; the medium-intensity bands in the range $270\text{--}290\text{ cm}^{-1}$ relate to the bond deformation vibrations of fluorozirconate groupings. The presence of Zr-F bridge and nonbridge bonds in spectra indicates the complexes formed to be unsymmetrical. The presence of compounds of zirconium in lower oxidation states in interaction products is also evidenced by IR spectra, which are in satisfactory agreement with literature data (Fig. 6). It should be noted that zirconium difluoride, which was obtained at the stoichiometric ratio of the ZrF_4 and Zr constituents in a potassium fluoride-lithium fluoride melt (50 mol % KF), turned out to be X-ray amorphous, therefore the authors identified it by IR spectroscopy [16].

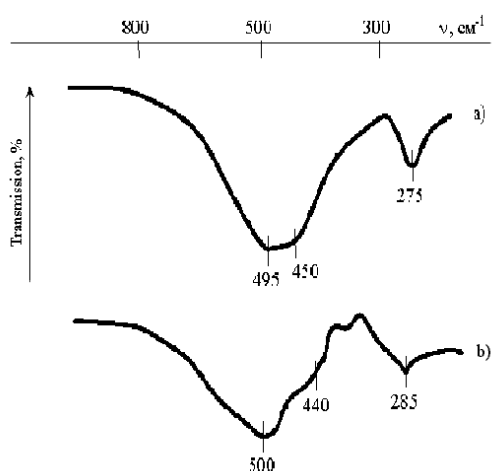
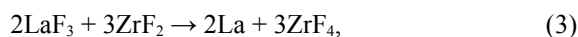


Fig. 6. IR spectra of products of interaction between zirconium tetrafluoride and metallic zirconium in the melts KF-LiF (a) [16] and NaF-ZrF₄ at the ratio ZrF₄ : Zr = 3 : 1 (b)

Thus, the interaction in the system NaF-ZrF₄-LnF₃-Zr (where Ln = La, Yb) may be represented by the following equations:



i.e. exchange reaction (1) is paralleled by the interaction of metallic zirconium with tetrafluoride to form zirconium difluoride (2), which then also takes part in the reduction of rare-earth fluoride to metal (3).

Investigation of the system NaF-ZrF₄-LnF₃-Na.

According to the results of thermographic investigations carried out, the interaction of rare-earth trifluoride with lead-sodium alloy is characterized by a broad thermo-effect in the temperature range $70 \dots 480^\circ\text{C}$. Endotherms of the melting of intermetallic compounds of sodium and lead of the compositions NaPb₃ and Na₃Pb₂ have been found on heating curves at 320 and 400°C . The interaction between rare-earth fluoride and metallic sodi-

um begins in the solid phase since the beginning of the exotherm on DTA curves is in the temperature range $70 \dots 90^\circ\text{C}$ and reaches a maximum at $(380 \pm 5)^\circ\text{C}$.

The results of an XPA of the interaction products of the system NaF-ZrF₄-LaF₃-Pb-Na showed that in the samples under investigation there are complicated compounds comprising sodium and zirconium fluorides (Na₃ZrF₇, Na₂ZrF₆) and ZrF_{2-x} ($1 > x > 0$), which is formed by interaction between metallic sodium and zirconium tetrafluoride and crystallizes in orthorhombic system, and metallic lanthanum of hexagonal system (Fig. 7).

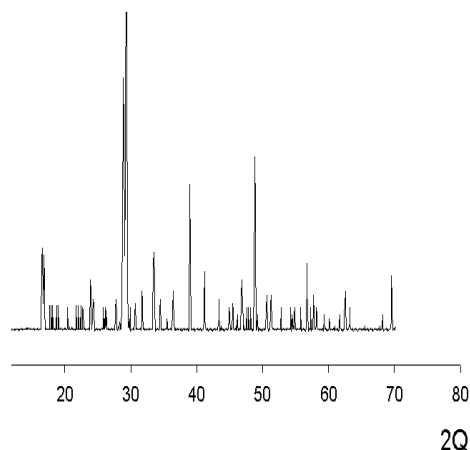


Fig. 7. Diffractogram of interaction products of a sample of the system NaF-ZrF₄-Pb-Na-LaF₃

It should be borne in mind that along with the reduction of rare-earth fluoride, the interaction of reducing metal with zirconium tetrafluoride, which is part of the solvent melt NaF-ZrF₄, occurs. This is supported by the results of an investigation of the system NaF-ZrF₄-Pb-Na at NaF-ZrF₄ : Na ratios of 1:1 to 3:1 (mol). The interaction between the constituents of mixtures is characterized by a broad exotherm with a maximum at $(380 \pm 5)^\circ\text{C}$. A number of endotherms of the melting of the intermetallic compounds NaPb₃ and Na₃Pb₂ have been found on DTA curves (Fig. 8, curve 1) at $(380 \pm 5)^\circ\text{C}$ and $(400 \pm 5)^\circ\text{C}$.

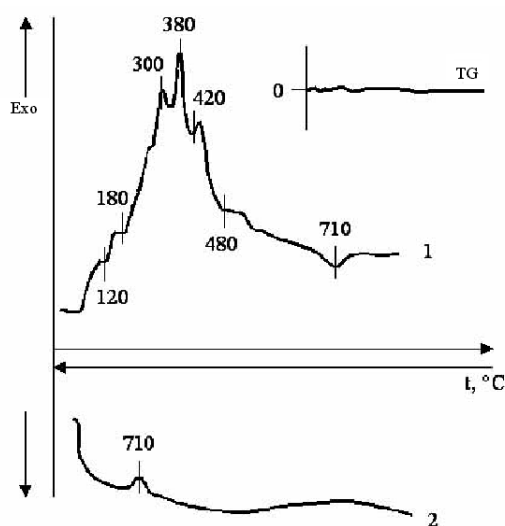


Fig. 8. Heating (1) and cooling (2) curves for a sample of the system $\text{NaF-ZrF}_4\text{-Pb-Na}$

As a result of the investigations carried out it has been found that metallic sodium reduces zirconium tetrafluoride in the NaF-ZrF_4 mixture to lower oxidation states in the temperature range $70\text{...}500^\circ\text{C}$ and increases the melting point of the solvent melt to 730°C .

The character of the interaction of the components of the systems under investigation in the case of cooling differs greatly from that considered above. The DTA curves exhibit in the temperature range $700\text{...}730^\circ\text{C}$ only a thermoeffect which corresponds to the endotherm of the melting of sodium fluoride-zirconium fluoride mixture (Fig. 8, curve 2).

The following compounds have been identified by XPA among the interaction products of the $\text{NaF-ZrF}_4\text{-Pb-Na}$ system: ZrF_2 , $\text{Na}_5\text{Zr}_2\text{F}_{13}$, Na_3ZrF_7 , Na_2ZrF_6 . The considerable increase in the melting point of sodium fluoride - zirconium fluoride mixture (710°C) may be attributed to the formation at the peritectic point of the compounds $5\text{NaF}\cdot 2\text{ZrF}_4$, which has a higher melting point as compared with the main compound $7\text{NaF}\cdot 6\text{ZrF}_4$ (520°C) of the original mixture.

The results of investigation of the interaction of rare-earth fluoride with lead-sodium alloy showed that the law governing reduction established manifests itself in the case of change of the reducing metal. That is the interaction of metallic sodium with rare-earth trifluoride and with the zirconium tetrafluoride of the solvent melt takes place at the same time to form compounds of zirconium in lower oxidation states and a rare-earth metal.

Thus, as a result of the research carried out, it has been found that the interaction of zirconium and sodium with rare-earth fluorides begins in the temperature range where the constituents of reaction mixtures are in the solid state. Zirconium (IV) and (II) compounds: Na_2ZrF_6 , $\text{Na}_5\text{Zr}_2\text{F}_{13}$, ZrF_2 ; complicated compounds comprising rare-earth trifluoride and sodium fluoride (NaLnF_4), and reduced lanthanides have been identified in the interaction products by physico-chemical methods of analysis. It has been found that the degree of reduction of rare-earth fluorides depends on sodium concen-

tration in lead-sodium alloy. It has been found that at a reducing metal concentration in the alloy of over 15 wt %, practically complete reduction of rare-earth metal from its fluoride takes place, whereas at even fourfold excess of zirconium the degree of reduction of rare-earth fluorides is no more than 33...35 wt %.

Comparison of the results of the work with the data, obtained earlier, on the interaction of rare-earth fluorides with metallic zirconium and sodium in a molten sodium fluoride-lithium fluoride mixture [7, 9] shows that the change of the cationic composition of reaction mixtures (NaF-LiF , NaF-ZrF_4) influences the stepwise character of exchange reactions between rare-earth fluorides and reducing metals. In the system NaF-ZrF_4 , sodium and zirconium reduce not only rare-earth fluorides but also zirconium tetrafluoride. Compounds of zirconium in lower oxidation states also show reducing ability with respect to rare-earth fluorides.

An interaction takes place between rare-earth fluorides and sodium and lithium fluorides to form complex compounds of the composition MLnF_4 (where $\text{M} = \text{Li, Na}$). Increase in the atomic number of rare-earth element does not affect the composition of these compounds.

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ВЗАИМОДЕЙСТВИЕ ФТОРИДОВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С МЕТАЛЛАМИ В РАСПЛАВЛЕННОЙ СМЕСИ ФТОРИДОВ НАТРИЯ И ЦИРКОНИЯ

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Приведены результаты исследований взаимодействия фторидов редкоземельных элементов (РЗЭ) с металлическим натрием и цирконием в расплавленной смеси фторидов натрия и циркония. Исследования выполнены методами дифференциально-термического (ДТА), рентгенофазового (РФА), ИК-спектроскопии и химического анализов. Показано, что металлический натрий и цирконий восстанавливают фториды РЗЭ в температурном интервале, когда составные компоненты реакционных смесей находятся в твердом состоянии, с образованием соединений циркония низших степеней окисления и редкоземельных металлов. Установлена прямолинейная зависимость температуры начала реакций обмена от химической природы галогенида РЗЭ: увеличение температуры плавления фторида РЗЭ приводит к повышению температуры начала взаимодействия. Степень восстановления фторидов РЗЭ металлами-восстановителями зависит от соотношения компонентов в исходной реакционной смеси.

ВЗАЄМОДІЯ ФТОРИДІВ РІДКІСНОЗЕМЕЛЬНИХ ЕЛЕМЕНТІВ З МЕТАЛАМИ В РОЗПЛАВЛЕНІЙ СУМІШІ ФТОРИДІВ НАТРІЮ ТА ЦИРКОНІЮ

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Приведені результати досліджень взаємодії фторидів рідкісноземельних елементів (РЗЕ) з металічним натрієм та цирконієм у розплавленій суміші фторидів натрію та цирконію. Дослідження виконані методами диференційно-термічного (ДТА), рентгенофазового (РФА), ІЧ-спектроскопії та хімічного аналізів. Показано, що металічний натрій та цирконій відновлюють фториди РЗЕ в температурному інтервалі, коли складові компоненти реакційних сумішей перебувають в твердій фазі, з утворенням сполук цирконію нижчих ступенів окислення та рідкісноземельних металів. Виявлена залежність температури початку реакцій обміну від хімічної природи галогеніду РЗЕ: зростання температури плавлення фториду РЗЕ призводить до підвищення температури початку взаємодії. Ступінь відновлення фторидів РЗЕ металлами-відновниками залежить від співвідношення компонентів у вихідній реакційній суміші.