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THERMOGRAPHIC RESEARCH OF THORIUM TETRAFLUORIDE–CESIUM FLUORIDE SYSTEM IN MELT

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Interreaction of ThF₄ and CsF in solution in the range of 700–900⁰C has been studied by thermographic means. It has been stated that in the system following chemical compounds are formed (that melt congruent without decay): Cs₃ThF₇ (T_m =765⁰C); CsThF₅ (825⁰C); Cs₃Th₂F₁₁ (842⁰C); CsTh₆F₂₅ (844⁰C).

Keywords: thorium tetrafluoride, cesium fluoride, cluster structure.

There is significant amount of works in literature that are dedicated to the research of interaction between fluorides of rare earth elements with alkali metals fluorides [1, 2]. But the works about interaction between thorium tetrafluoride with alkali metals fluorides are studied insufficiently.

Experimental Part. In the present article the interaction between thorium tetrafluoride with cesium fluoride by methods of DTA and RF analyses was studied. For this purpose thorium tetrafluoride was synthesized by the method described in [3]. Cesium fluoride of chemically pure brand was blasted and dried at $100-110^{\circ}C$ to withdraw the crystallized water. For building the diagram of thorium tetrafluoride–cesium fluoride system the curve of heating and the curve of cooling of the alloys of different compounds were recorded on the MOM [4] system derivatograph and the radiographic analysis was carried out on the DRON-2 radiograph with CuK_{α} -radiation and with the markers of the angles through 1[°]. Because the samples of the fluorides are hygroscopic, they were protected from the touch with the air by radio amorphous polymeric film.

In the system of thorium tetrafluoride–cesium fluoride the formation of four chemical compounds is mentioned, which melt congruently (Fig. 1):

$$\begin{aligned} &3\text{CsF} \cdot \text{ThF}_{4}, \quad T_{\text{m}} = 765^{\circ} C; \\ &\text{CsF} \cdot \text{ThF}_{4}, \quad T_{\text{m}} = 825^{\circ} C; \\ &3\text{CsF} \cdot 2\text{ThF}_{4}, \quad T_{\text{m}} = 842^{\circ} C; \\ &\text{CsF} \cdot 6\text{ThF}_{4}, \quad T_{\text{m}} = 844^{\circ} C. \end{aligned}$$

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Fig. 1. Diagram of the system's meltability ThF₄–CsF: $S_1 - 3$ CsF·ThF₄; $S_2 -$ CsF·ThF₄; $S_3 - 3$ CsF·2ThF₄; $S_4 -$ CsF·6ThF₄.

All the compounds go through the poly amorphous transformation. Eutectic points of system: E_1 (582°C, 12 mol % ThF₄); E_2 (685°C, 75 mol % CsF); E_3 (775°C, 55 mol % CsF); E_4 (770°C, 55 mol % ThF₄); E_5 (765°C, 70 mol % ThF₄).



Fig. 2. Stroke radiogram of the alloys of the compound ThF₄–CsF system.

On the Stroke radiogram (Fig. 2) it is clear that compounds Cs_3ThF_7 , $CsThF_5Cs_3Th_2F_{11}$, $CsTh_6F_{25}$ are individual.

Conclusion. In this system the new chemical stable compounds are forming, which have cluster structure [5]. As it is already known, in classic coordinating chemistry a mononuclear compound has been considered, where the central ion of the metal is surrounded by ligand, whose formation is being explained by the theory of Werner. But it was cleared up that there could be formed such complex compounds, where few cations of the same metal could form multinuclear coordinating compounds [2, 3], as a result of which the distance of metal-metal is very short and the ligands are surrounded by few central ions of metals. This kind of multinuclear coordinating compounds are called cluster compounds, which is inherent in *d*- and *f*-block elements. It is found out that some catalysts have cluster structure and accomplish the fixing function of the atmosphere's nitrogen.

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