ISSN 1066-3622, Radiochemistry, 2011, Vol. 53, No. 5, pp. 491–493. © Pleiades Publishing, Inc., 2011.
Original Russian Text © M.B. Seregin, A.P. Parshin, A.Yu. Kuznetsov, L.I. Ponomarev, S.A. Mel'nikov, A.A. Mikhalichenko, A.A. Rzheutskii, R.N. Manuilov, 2011, published in Radiokhimiya, 2011, Vol. 53, No. 5, pp. 416–418.

Solubility of UF_4, ThF_4, and CeF_3 in a LiF–NaF–KF Melt

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Received December 27, 2010

Abstract—The solubility of UF_4, ThF_4, and CeF_3 in fluoride melt of the composition 45 mol % LiF–12 mol % NaF–43 mol % KF in the temperature interval 773–973 K was determined. The solubility of the fluorides increases with an increase in the melt temperature. The CeF_3 solubility in the LiF–NaF–KF system is high: 19.9 mol % at 923 K and 23.3 mol % at 973 K. Experimental data on the solubility of CeF_3 (PuF_3 imitator) were compared to the calculated data on the PuF_3 solubility in the LiF–NaF–KF melt. The results showed that CeF_3 can be considered as PuF_3 imitator in FLINAK melt.

Keywords: uranium tetrafluoride, thorium tetrafluoride, cerium trifluoride, fluoride melts, solubility

DOI: 10.1134/S1066362211050079

The performance of a molten salt reactor (MSRs), in particular, of a transmutation reactor (MSTR) [1, 2], depends not only on its design and nuclear-physical characteristics, but also on the choice of a fuel salt (FS). The commonly chosen fuel salts are low-melting fluoride systems like $^7LiF–BeF_2$, $NaF–ZrF_4$, $^7LiF–NaF–BeF_2$, etc. The fuel salt and its components should meet the following main requirements: low neutron capture cross section; low melting point; low cost of fuel salt; relatively low toxicity; high solubility of fluorides of U, Pu, Am, Cm, and fission products (FPs) in the melt; and corrosion resistance of structural materials in the fuel salt under the conditions of MSR operation.

Search for a fuel salt for a molten salt reactor that would fully meet the nuclear-physical and physicochemical requirements and could be efficiently regenerated is still continued. One of promising fluoride compositions for use in an innovation MSTR is the LiF–NaF–KF system.

Today, among all the promising fuel compositions considered for MSR, the LiF–NaF–KF system is the least studied. The corrosion resistance of a number of structural materials in the LiF–NaF–KF melt was studied. The most resistant in the FLINAK system are alloys with high Ni content and low Cr content, in particular, Ni-203 and Hastelloy-N [3].

With FLINAK system, it is possible to perform electrochemical processes for the FS decontamination from the accumulated FPs. In particular, electrolysis of this system allows separation of UF_4 and trifluorides of Nd, Gd, and Eu [4].

Data on the solubility of actinide and fission product fluorides in the LiF–NaF–KF system are practically lacking. The lack of such data complicates evaluation of the applicability of the LiF–NaF–KF melt as a fuel salt for MSTR and development of a concept of the MSTR nuclear fuel cycle.

In this study we performed systematic measurements of the solubility of UF_4, ThF_4, and CeF_3 in the system 45 mol % LiF–12 mol % NaF–43 mol % KF (T_m = 725 K) in the temperature interval 773–973 K.

Uranium, thorium, and cerium fluorides were prepared by hydrofluorination of the corresponding metal oxides of ultrapure grade. Lithium, sodium, and potassium fluorides were prepared according to [5].

The procedure for preparing a fuel salt melt consisted in thorough mixing of the components in the required proportion, followed by fusion under Ar at 973–1023 K in a graphite crucible. The fluorides being studied were taken as preliminarily fused cylindrical specimens. Experiments were performed in a hermetically sealed retort with controllable atmosphere. The

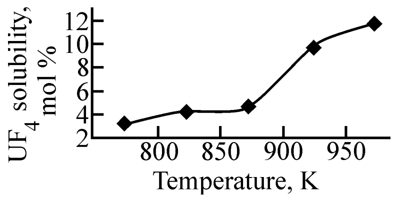

Fig. 1. Temperature dependence of the UF_4 solubility in 45 mol % LiF–12 mol % NaF–43 mol % KF melt.

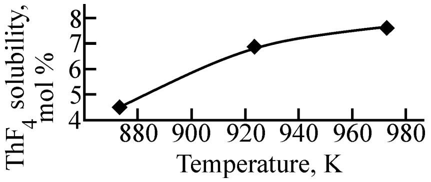

Fig. 2. Temperature dependence of the ThF_4 solubility in 45 mol % LiF–12 mol % NaF–43 mol % KF melt.

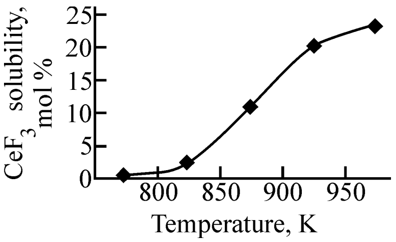

Fig. 3. Temperature dependence of the CeF_3 solubility in 45 mol % LiF–12 mol % NaF–43 mol % KF melt.

melt temperature was maintained with an accuracy of ±0.5 K.

The procedure for determining the solubility of the fluorides consisted in fusion of a weighed portion of the prepared homogeneous mixture LiF–NaF–KF, heating of the melt to the required temperature, and keeping of each cylindrical specimen, taken separately, in this melt for 12 h. The procedure for determining the solubility of fluorides is described in more detail elsewhere [6].

The U content of the melt was determined by Sakharov's method [7]; the Th content, gravimetrically [8]; the Ce content, by titration [8]; and the F content, according to [9]. The relative uncertainty of the determination of U, Th, and Ce was ±0.5%.

The experimental data on the UF_4 solubility in 45 mol % LiF–12 mol % NaF–43 mol % KF melt in the temperature interval 773–973 K are plotted in Fig. 1.

The UF_4 solubility increases from 3.18 mol % at 773 K to 11.7 mol % at 973 K. In accordance with data of Fig. 1, the temperature dependence of the UF_4 solubility can be subdivided into two temperature intervals. In the interval 773–873 K, the temperature dependence of the UF_4 solubility can be described by the equation $C(UF_4) = 0.015T - 8.30$, $R^2 = 0.935$, and in the interval 873–973 K, by the equation $C(UF_4) = 0.070T - 56.10$, $R^2 = 0.941$.

As seen from Fig. 1 and the above equations, in the temperature interval 873–973 K an increase in temperature leads to a sharper increase in the UF_4 solubility than in the interval 773–873 K.

The ThF_4 solubility in 45 mol % LiF–12 mol % NaF–43 mol % KF melt at 773 and 825 K is low: 0.03 and 0.05 mol %, respectively. Figure 2 shows the experimental data on the ThF_4 solubility in the temperature interval 873–973 K in which the ThF_4 solubility considerably increases: from 4.52 mol % at 873 K to 7.63 mol % at 973 K. The temperature dependence of the solubility can be described by the linear equation $C(ThF_4) = 0.031T - 22.38$, $R^2 = 0.928$.

Barton et al. [10] studied the CeF_3 solubility in $LiF–BeF_2$ melts with different component ratios and compared it to the PuF_3 solubility in the similar melts. They found that the difference between the CeF_3 and PuF_3 solubilities in a wide interval of BeF_2 concentrations is approximately constant, 14% on the average. Barton et al. concluded that cerium trifluoride can be taken as plutonium trifluoride imitator in $LiF–BeF_2$ melts. It cannot be judged unambiguously whether this conclusion can be applied to the LiF–NaF–KF melt, but preliminary data show that CeF_3 can be used for estimating the PuF_3 solubility.

We examined the influence of temperature on the CeF_3 solubility in the LiF–NaF–KF melt in the temperature interval 773–973 K. The results are shown in Fig. 3. The CeF_3 solubility increases from 0.42 mol % at 773 K to 23.3 mol % at 973 K. The temperature dependence of the CeF_3 solubility can be satisfactorily described by the linear equation $C(CeF_3) = 0.126T - 99.47$, $R^2 = 0.960$.

As noted above, the experimental data on the solubility of plutonium fluorides in LiF–NaF–KF melt are practically absent. Beneš and Konings [11] made an attempt of computational modeling of the PuF_3 solubility in 43.9 mol % LiF–14.2 mol % NaF–41.9 mol % KF melt. They calculated the equations for the temperature dependence of the PuF_3 solubility: $\log S = -1.416 - 2.670 \times 10^{-3}T + 3.859 \times 10^{-6}T^2$ (interval 823–

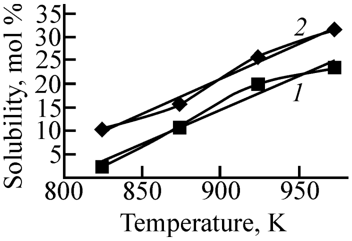

Fig. 4. Comparison of the (*1*) experimental temperature dependence of the solubility of CeF_3 (PuF_3 imitator) and (*2*) data for PuF_3, calculated using the equations from [11].

938 K); $\log S = -1.160 + 6.768 \times 10^{-4}T$ (interval 938–1023 K).

In Fig. 4, the experimental data on the solubility of CeF_3 as PuF_3 imitator were compared to the calculated data on the PuF_3 solubility in the LiF–NaF–KF melt in the temperature interval 823–973 K. In addition, we present in Fig. 4 the linear approximations of curves *1* and *2*. As follows from Fig. 4, linear approximations of curves *1* and *2* are practically parallel and in the temperature interval 823–973 K can be described with a high accuracy by the following equations. For curve *1*: $C(CeF_3) = 0.145T - 116.13$, $R^2 = 0.968$; for curve *2*: $C(PuF_3, \text{calculation}) = 0.149T - 113.13$, $R^2 = 0.987$.

As can be seen, the slopes of the straight lines are practically equal (differ by only 0.4%); therefore, it can be expected that CeF_3 will adequately imitate PuF_3 in the LiF–NaF–KF melt also.

The results of studies [10, 12–14] in which the solubility of PuF_3 and CeF_3 in $2LiF–BeF_2$ melt was examined also count in favor of this assumption. The PuF_3 solubility (mol %) at 898 K was 0.659 [12], 0.52 [13], and 0.72 [14], and at 923 K, 0.83 [14]. Barton et al. [10] also studied the CeF_3 solubility in $2LiF–BeF_2$ melt and obtained the values of 0.56 mol % at 873 K and 0.90 mol % at 923 K. On the basis of the data obtained, it can be expected that the PuF_3 solubility in the LiF–NaF–KF system will be considerably higher than in the $2LiF–BeF_2$ system.

The main result of this study is that we found high solubility of CeF_3 in the LiF–NaF–KF melt. We also measured the solubility of UF_4 and ThF_4 in the interval 773–973 K and found that CeF_3 can be used as PuF_3 imitator in performing studies in the LiF–NaF–KF system. Measurement of the PuF_3 solubility in reference temperature points will furnish information on the PuF_3 solubility in the LiF–NaF–KF melt in a wide temperature interval.

ACKNOWLEDGMENTS

The study was supported by the Rosatom State Corporation, State Contract no. H.4f.45.03.09.1037 of March 5, 2009.

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