

Chemistry of Molten Salt Reactor Fuel Salt Candidates

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INTRODUCTION

Molten salt reactor (MSR) concepts are based on using a molten salt mixture as a primary nuclear reactor coolant, while the fuel can be either directly dissolved in the coolant or can be solid. MSRs can be operated with (epi)thermal [1] or fast neutron spectra [2], as simple convertors or breeder reactors utilising, e.g., the ^{232}Th - ^{233}U cycle [3], but also as accelerator-driven sub-critical reactors [4] or transuranium elements (TRU) burners [5]. The main advantages of the MSRs using a liquid molten salt fuel resides in the enhanced safety features such as a large negative temperature coefficient of reactivity due to a high thermal expansion, low atmospheric pressure in the core during the operation and no need of transport and fabrication of new fuel elements in the case of closed fuel cycle option [6]. In addition, the liquid fuel brings possibility of continuous fission-product removal via physical and pyrochemical processes which brings flexibility in the fuel cycle [7].

In the last years, development of MSR technology is on the increase in many countries [8] and since 2002, the MSR concept is included to the Generation IV initiative [9]. Since 2001, the European Commission (EC) carries on coordinated R&D activities on the MSR concept within the EC/EURATOM framework programmes [10]. Several projects have been funded exploring the feasibility and safety of the Molten Salt Fast Reactor (MSFR) concept studied in Europe [2]. MSFR is based on a non-moderated epi-thermal neutron spectrum with its fuel dissolved in a fluoride molten salt carrier and utilising a closed thorium fuel cycle [11].

Basic thermodynamic and electrochemical data of pure actinide fluorides and their mixtures are required for the design and safety assessment of any presently studied molten salt reactor concept based on molten fluoride salt fuel. The present work is summarising the recent research in this field carried out at Joint Research Centre (JRC) of the European Commission. It is particularly focused on the synthesis and characterisation of pure actinide fluorides UF_4 , ThF_4 and PuF_3 needed for the experimental assessment of the thermodynamic properties of the MSR fuel salt candidates. In addition, the recent achievements of these studies are presented, e.g., re-determination of the UF_4 melting point and measurement of the novel thermodynamic data of PuF_3 - LiF system. Part of the work has been published in [12].

RESULTS

Synthesis of actinide fluorides

This part describes synthesis and characterisation of pure UF_4 , ThF_4 and PuF_3 from the respective oxides. The work was carried out using a facility for hydrofluorination of actinides described below. All chemicals and samples were stored and treated in a glove-box under a pure Ar atmosphere with oxygen and moisture content < 1 ppm.

Experimental equipment

The unique installation for synthesis of pure actinide fluorides was originally designed and installed at JRC-Karlsruhe and it is using pure HF gas as the fluorination agent. It consists of a glove box kept under pure inert Ar gas atmosphere, a high temperature fluorination reactor and a HF supply gas line connected to the glove box. The fluorination apparatus consists of a horizontal tube reactor inserted in a resistance furnace enabling work at temperatures up to 1200°C. The equipment is in detail described in [12].

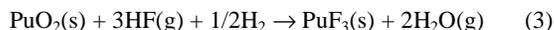
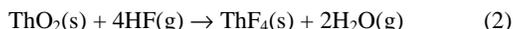
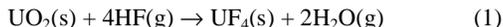
Initial materials

In order to enhance the kinetics of the fluorination reaction, a special attention was paid to the preparation of the initial oxide materials, UO_2 , ThO_2 and PuO_2 . The powder should have the highest possible surface to increase the reactivity and in addition, especially in case of uranium, a stoichiometric UO_2 was needed, otherwise a mixture of uranium fluorides of different oxidation states would be achieved.

The most important step to achieve the high reactive powder is thermal decomposition of the respective oxalate and its conversion to oxide at relatively low temperatures, e.g. 800°C for U and Th [12], 600°C for Pu. The used oxide powders had crystal sizes 140, 30 and 45 nm for U, Th and Pu, respectively.

Procedures for the syntheses

The syntheses were based on a solid-gas reaction between the stoichiometric oxides with pure HF gas at elevated temperatures according to the reactions (1-3):



The oxide was inserted into the Inconel boat in several batches from 1 to 5 grams and placed in the central homogeneous heating zone of the horizontal fluorination reactor. The reactor was gas tight-closed, evacuated to an absolute pressure of 1 mbar and heated to the desired temperatures of 450, 600 and 550°C for U, Th and Pu, respectively. Pure HF gas was then introduced into the reactor and after reaching a slight overpressure, the gas was flushed through the reactor in order to reach an overall HF gas molar excess over the reaction stoichiometry about 3-4. In case of Pu, the reactor was consequently filled and flushed with Ar-H₂(6%) gas to complete the reduction of PuF₄ to the desired PuF₃ product. In case of UO₂ fluorination, two consequent runs had to be performed to achieve a pure product, free from any residual oxide.

Characterisation of the products

The synthesised fluorides were characterised by the following techniques: gravimetric mass balance of the reaction, X-ray diffraction (XRD) for the qualitative phase analysis, differential scanning calorimetry (DSC) for the melting temperature determination and in case of Th and Pu also by ICP-MS for the level of impurities.

In all cases, homogeneous fine powders were obtained, having dark green, white and purple-violet colours for U, Th and Pu, respectively. The photos of the final products are shown in Fig. 1. The mass balance indicated very high conversion efficiency with a yield of 99.6% for U and Th and 99.8% for Pu.



Fig. 1. Photos of the final products UF₄, ThF₄ and PuF₃ (from left to right)

The XRD patterns indicated for each case a single phase composition of the samples, as shown in Fig. 2 for the case of the UF₄ product. The detail in the inset in the right upper corner of the figure shows a comparison of the region from 26° to 32° 2θ obtained after first and second runs of the fluorination. Actinide dioxides have the most intensive diffraction peak around 28.2° 2θ, while the fluorides have no peaks in this region. Therefore, it is the most significant region for detection of possible traces of the oxide in the products. The Rietveld refinement of the pattern after first

fluorination revealed about 1 wt.% of UO₂ in the powder. After the second run, pure single phase UF₄ pattern was observed. For Th and Pu, one fluorination run was sufficient to obtain fully oxygen free product.

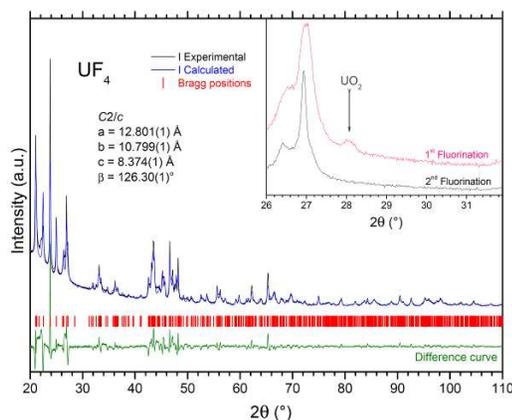


Fig. 2. Rietveld refinement of XRD pattern obtained after the second UO₂ fluorination.

Conventional DSC technique was used for the melting temperature evaluation, which is a significant indicator of purity. The melting temperature determination for UF₄ based on the DSC heat flow signal is shown in Fig. 3 as a typical example.

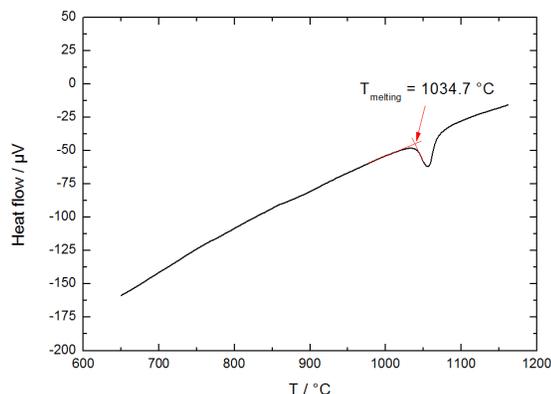


Fig. 3. Melting temperature determinations of UF₄ by DSC

The melting temperature of UF₄ was assessed to be 1034.7 (±3.0)°C, which is only slightly lower compared to the literature value 1036°C. The melting point published by Sheil [13] is a value extrapolated and corrected for UO₂ impurities, which were presented in his sample, and not obtained by direct characterisation of pure UF₄. Since the XRD analysis did not reveal any impurities and the DSC curve showed clearly single peak upon melting point, which indicated purity of the sample >99 wt.%, the value 1034.7 (±3)°C was suggested as a novel melting point of UF₄ [12].

The melting temperature of ThF₄ was found at 1111.4 (±3)°C, which is in a very good agreement with the literature value 1110.0°C [14]. The DSC heat flow signal also showed only one peak with no shoulder, indicating a single phase material. Due to too high melting temperature, PuF₃ could not be measured alone and its mixtures with LiF were studied, as described in detail in the following section.

The ICP-MS analyses of ThF₄ and PuF₃ products yielded no impurity at concentration higher than 0.1 wt.%, while in case of Pu, the most important contaminant was U at a concentration of 0.069±0.008 wt.% and for Th it was sulphur at a concentration of 0.028±0.008 wt.%. In both cases, the product was found >99.9% metal base pure.

Novel thermodynamic data of PuF₃-LiF system

Within the above mentioned MSFR reactor concept [2], plutonium in the form of trifluoride is considered as a possible fissile material for the reactor fuel and LiF-ThF₄ eutectic mixture as a main carrier fuel salt. Therefore the thermodynamic assessment of the PuF₃-LiF system is fundamental for the development of the MSFR. Since only one experimental study was found in literature on the PuF₃-LiF phase diagram [15], the goal of the work was to carry out an independent study of the phase equilibria data and to extend the range of the existing experimental values.

Experimental

The phase transition temperatures of samples with PuF₃ content up to 60 mol% were measured by the DSC technique. The apparatus was a Setaram Multi-detector High Temperature Calorimeter (MHTC 96) equipped with a DSC sensor with B-type thermocouple. The PuF₃-LiF samples of approximately 60 mg each were prepared mixing the end-members in the corresponding ratios in an agate mortar and encapsulated in stainless steel crucible with a nickel liner for chemical compatibility [16]. The ratio PuF₃-LiF (21-79 mol.%) [17] was taken as reference eutectic composition in the present work.

The experimental chamber of the DSC was connected to a helium gas line and was purged and evacuated twice before each experiment. The temperature program was kept the same for each sample and consisted of two ramps up and down at 10 K/min. For the thermodynamic assessment only the second ramp was considered as the first one was aimed at getting a perfect mixing between the end-members. The measured values were corrected by temperature calibration based on melting points of several reference metals (Sn, Pb, Zn, Al, Ag, Cu).

PuF₃-LiF phase diagram

Eleven different PuF₃-LiF mixtures having PuF₃ content from 7.5 to 60.0 mol. % were measured by DSC and the phase transition temperatures were assessed. As

confirmed by the XRD analysis, PuF₃ and LiF do not form any stable intermediate compounds during heating up to 1300°C, in agreement with the DSC results, which shows no more than two events for a single ramp. These phase transition events correspond to the eutectic melt (solidus) and the complete melting (liquidus).

The solidus point can be derived from the onset temperature of the first peak that appears, shown in Fig. 4.

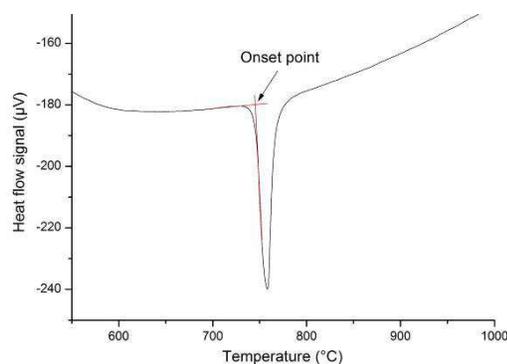


Fig. 4. Determination of the melting temperature of the eutectic composition PuF₃-LiF (21-79 mol%)

For the determination of the liquidus point, different approaches were used. The DSC heat flow signal showed either a second broad peak or a change of slope. In the former case, the liquidus point was taken as the offset temperature of the peak. The latter case was detected for all samples having PuF₃ content higher than the eutectic composition, which caused that the liquidus event was affected by the continuous enthalpy effect. In this case, the liquidus point was taken from the intersection of the extrapolated lines before and after the slope change.

The phase transition temperatures obtained in this work are summarised in Table I and shown in Fig. 5 as the experimental points in the thermodynamically assessed phase diagram calculated in [17] and are in excellent agreement with the published experimental values [15].

TABLE I. Phase transitions of the PuF₃-LiF system

Composition (mol.% Pu)	Eutectic T (K)	Liquidus T (K)
7.50	1016	1094
15.00	1015	1063
21.00	1018	-
25.02	1014	1014
29.83	1015	1161
35.02	1012	1232
41.01	1009	1290
44.81	1016	1328
49.76	1011	1389
54.90	1008	1438
59.99	1004	1469

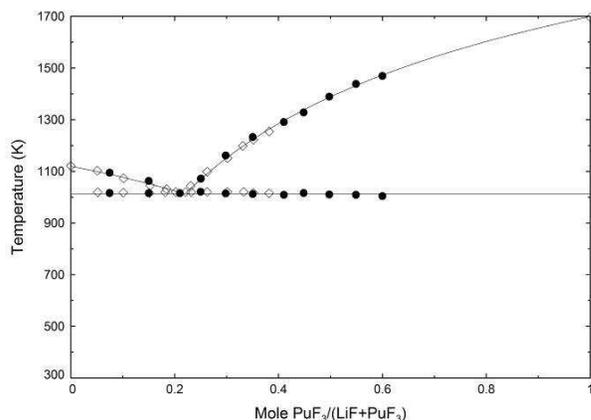


Fig. 5. The PuF_3 -LiF phase diagram. (●) Data measured in this study (± 10 K). (◇) Data from [15]. Solid line, data calculated in [17].

CONCLUSION

The synthesis of phase pure (>99%) UF_4 , ThF_4 and PuF_3 has been demonstrated by fluorination of the oxides by HF gas. The purity has been verified by XRD phase analyses in a combination with conventional DSC melting temperature determination. Based on the results and uncertainties of these analyses, all the fluorination products were assumed to be > 99% phase pure.

For the first time, the melting point of UF_4 was determined directly by a calorimetric technique on a phase pure sample (> 99%) and was found at $1034.7 (\pm 3)^\circ\text{C}$.

The synthesised PuF_3 was then used for experimental assessment of the phase equilibria of the PuF_3 -LiF system. The obtained phase transition temperatures of compositions with PuF_3 content in the range 0-40 mol% are in a very good agreement with the experimental results and the values for the compositions with PuF_3 content in the range 40-60% have been measured for the first time, confirming experimentally the phase diagrams calculated in the earlier studies. The calculated values using the previously published thermodynamic model are in excellent agreement with the experimental value measured in the present work, and no re-optimization of the phase diagram is needed.

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