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Solid state reactions of UO_2, ThO_2 and their mixed oxides with sulphates of potassium

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Abstract

Solid state reactions of UO_2, ThO_2 and their mixed oxides $(U_x, Th_{1-x})O_2$, where $x = 0.05$, 0.25 and 0.50, were carried out with $KHSO_4, K_2S_2O_8$ and $K_2S_2O_7$ at 400°C, 600°C and 900°C with an aim to study the formation of various products and to investigate their dissolution behaviour. The products obtained at 400°C by heating UO_2, ThO_2 and their mixed oxides with potassium salts were identified as $K_4U(SO_4)_4, K_4Th(SO_4)_4$ and $K_4(U_x, Th_{1-x})(SO_4)_4$, respectively. The products formed at different temperatures were found to be soluble in 2M HNO_3 or H_2SO_4. From the solution of the dissolved products of the mixed oxides, thorium was separated quantitatively by precipitating it as thorium oxalate. X-ray, thermal and chemical methods were used to characterise the products formed at various temperatures. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In nuclear technology, dissolution of nuclear fuel materials in a suitable medium is an essential requirement for fuel reprocessing and for accurate and precise determination of their constituents by chemical analysis. Treating fuel materials with fused salts is one of the methods for bringing them in to the soluble form. The application of molten salt processes to nuclear fuel has been under study for a long time. The high temperature reactions (both in melts and solid state) of uranium oxides with carbonates, oxides, per- and super oxides, chlorides, sulphates, nitrates under oxidising and non-oxidising conditions have been critically reviewed by Griffiths and Volkovich [1].

In a sulphate medium, the relatively low melting point of alkali metal bisulphates and alkali metal pyrosulphates suggested that these compounds may be useful reactive molten solvents. Brambilla and Facchini [2] considered alkaline sulphate eutectic mixtures, melting at much lower temperatures than those of pure components, as a means of performing dissolution of nuclear fuel for irradiated fuel elements such as UO_2 and UO_2–PuO_2, both in powder as well as in ceramic pellet form. The carbonate melt containing sodium sulphate was used to react UO_2, resulting in the formation of sodium uranate [3]. Dissolution of uranium dioxide in potassium pyrosulphate [4] and $Na_2S_2O_7$–$K_2S_2O_7$ [5] melts has been suggested as a possible head end process in reprocessing oxide nuclear fuels. Milner et al. [6] recommended fusion with NH_4HSO_4 for the dissolution of PuO_2 or PuO_2–UO_2 samples. Identification of various reaction products formed during the solid state reaction of fuel oxides with $(NH_4)_2SO_4$ [7,8] was helpful in knowing the temperature and minimum proportion of the salt required for bringing the oxides in soluble form.

In the uranium oxide and mixed oxide fuel $(U, Th)O_2, UO_2$ is readily soluble in pure nitric acid whereas ThO_2 is soluble in concentrated nitric acid only if fluoride ions are present as a catalyst. Since UO_2 and ThO_2 form a solid solution in the full range of 0–100%, the dissolution of mixed oxide is a difficult task. In the present study, solid state reactions of UO_2, ThO_2 and their mixed oxides were carried out with $KHSO_4$, $K_2S_2O_8$ and $K_2S_2O_7$, with a view to investigate the formation of products at different temperatures and to examine their dissolution characteristics.

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2. Experimental

2.1. Sample preparation

UO_2 was prepared by equilibrating U_3O_8 (nuclear grade) in an atmosphere of Ar + 7% H_2 at 800°C for 4–5 h. ThO_2 was obtained by the decomposition of thorium oxalate in air at 800°C. Mixed oxides of the compositions $(U_x, Th_{1-x})O_2$ with $x = 0.05, 0.25$ and 0.50 were prepared by coprecipitating U and Th with NH_4OH from their nitrate solutions mixed in the required proportions. The hydroxides were filtered, dried and heated in Ar + 7% H_2 at 800°C for 4–5 h. All these oxides were further heat treated at 1200°C in an inert atmosphere of argon for 3–4 h. UO_2, ThO_2 and $(U_x, Th_{1-x})O_2$ were mixed separately with $KHSO_4, K_2S_2O_8$ and $K_2S_2O_7$ (all available in G.R. grade) in atom ratio of U or/and Th to K of 1:4. All the potassium salts and their mixtures with UO_2, ThO_2 and $(U_x, Th_{1-x})O_2$ were dried in vacuum at 100°C for 8–10 h. before their use. The mixtures were well ground using a pestle and mortar and heated in platinum boats in a furnace in air atmosphere at various temperatures.

2.2. Instrumental analysis

Thermograms of $KHSO_4, K_2S_2O_8$ and $K_2S_2O_7$ and reaction mixtures of all three potassium salts with UO_2, ThO_2 and their mixed oxides were taken on an ULVAC thermoanalyzer, recording both thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously. The samples were heated in a thermoanalyser in platinum cups at a heating rate of 10°C/ min in a flowing air stream. Preheated alumina was used as the reference material for DTA measurements.

X-ray powder diffraction (XRD) patterns of the heated products were recorded on Diano X-ray diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm).

2.3. Chemical analysis

All the heated products formed at different temperatures were treated with 2M H_2SO_4 or HNO_3.

The chemical analyses for total uranium, in the heated products formed at various temperatures, were carried out by redox titrimetry following Davies and Gray [9]. The weighed aliquots of the sample were dissolved in 1–2 M nitric acid. Uranium mainly present as U(VI) in the aliquot was reduced using Fe(II) solution in excess, in 10 M H_3PO_4. The excess of Fe(II) was destroyed selectively by adding HNO_3 containing Mo(VI) as catalyst. U(IV) thus formed was titrated against standard potassium dichromate solution using a potentiometric end point detection technique.

Thorium in the heated products was analysed by EDTA titrimetry using xylenol orange as indicator [10]. In the weighed aliquot of thorium solution, 1:1 NH_4OH was added drop by drop while stirring continuously, to get the pH between 2 and 3. Thorium was then titrated against standard EDTA solution using xylenol orange indicator.

3. Results and discussion

3.1. Thermal studies of potassium salts

The DTA curve of $KHSO_4$ in air showed two peaks at 180°C, one due to a solid-solid phase change and the other at 210°C, due to the melting of the salt. Its TG curve showed mass loss due to decomposition to $K_2S_2O_7$ between 250°C and 650°C [11]. The TG curve of $K_2S_2O_8$ showed a sudden mass loss around 200°C accompanied by a sharp exothermic DTA peak. The sharp DTA peak is due to the composite effect of endothermic conversion of $K_2S_2O_8$ to $K_2S_2O_7$, involving cleavage of the O–O bond in persulphate accompanied by a kinetically fast exothermic reaction between the oxygen atoms liberating a large amount of heat to form O_2 molecules [12].

The DTA curve of $K_2S_2O_7$ gave two endothermic peaks at 330°C and 415°C, due to the $\alpha \rightarrow \beta$ structural transition of $K_2S_2O_7$ and its melting respectively. Further heating of $K_2S_2O_7$ up to 900°C leads to the formation of K_2SO_4, as confirmed by mass loss and XRD.

3.2. Reaction of UO_2 with $KHSO_4, K_2S_2O_8$ and $K_2S_2O_7$

Thermograms of the reaction mixtures of UO_2 with all the three salts gave mass loss above 200°C. Fig. 1 shows TG and DTA curves of the reaction mixture of UO_2 and $KHSO_4$ with U to K atom ratio of 1:4. The TG curve showed mass loss in two steps, between 200–325°C and 440–650°C, both accompanied by endothermic

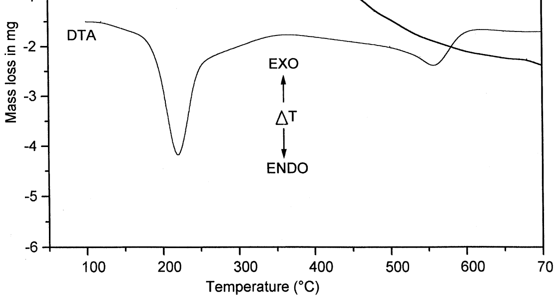

Fig. 1. TG and DTA curves of $UO_2 + 4KHSO_4$.

DTA peaks at 225°C and 550°C, respectively. The first DTA peak is due to the combined effect of melting of $KHSO_4$ and its reaction with UO_2. Isothermal heating of the mixture of $KHSO_4$ and UO_2 at 400°C led to the identification of the product $K_4U(SO_4)_4$ according to Eq. (1)

$$4KHSO_4 + UO_2 \rightarrow K_4U(SO_4)_4 + 2H_2O \qquad (1)$$

Further isothermal heating of the reactants at 600°C led to the decomposition of $K_4U(SO_4)_4$ to form $K_4UO_2(SO_4)_3$. The second peak in the DTA curve at 550°C was due to the decomposition of $K_4U(SO_4)_4$. The mass loss observed on isothermal heating of the reactants at 400°C and 600°C were in agreement with the formation of two sulphate compounds (Table 1). $K_4U(SO_4)_4$ and $K_4UO_2(SO_4)_3$ were further characterised by XRD powder patterns. The X-ray data of $K_4U(SO_4)_4$ was indexed on a triclinic system, cell parameters based on cell parameters of $(NH_4)_4U(SO_4)_4$ [7]. The cell parameters are given in Table 2. The X-ray data of $K_4UO_2(SO_4)_3$ agreed with the data reported earlier [13].

Fig. 2 shows the TG and DTA curves of the reaction mixture of $UO_2 + 2K_2S_2O_8$. The TG curve showed mass loss in two steps between the temperature range of 200–290°C and 450–640°C. The DTA curve showed a sharp exothermic peak at 215°C and three endothermic peaks at 335°C, 405°C and 550°C. The exothermic peak is due to the liberation of molecular oxygen during the conversion of $K_2S_2O_8$ to $K_2S_2O_7$, as observed in the case of pure $K_2S_2O_8$. The peaks at 335°C and 405°C were due to a phase transformation and melting of $K_2S_2O_7$, respectively. The reaction of UO_2 with $K_2S_2O_7$ at 400°C also led to the formation of $K_4U(SO_4)_4$, according to the reaction given in Eqs. (2) and (3). The products analysed by mass loss and XRD are given in Table 1.

Table 2
Cell parameters of $K_4U(SO_4)_4$ and $K_4Th(SO_4)_4$

Cell parameter	$K_4U(SO_4)_4$	$K_4Th(SO_4)_4$
a (nm)	1.8322 (7)	1.8346 (11)
b (nm)	0.9872 (5)	0.9939 (7)
c (nm)	1.4163 (7)	1.4202 (11)
α (°)	135.36 (2)	135.55 (3)
β (°)	110.60 (4)	110.72 (7)
γ (°)	76.32 (4)	76.05 (7)
Z	4	4
$\rho_{(calc.)}$ (g cm^{-3})	2.75	2.71

$$2K_2S_2O_8 \rightarrow 2K_2S_2O_7 + O_2\uparrow \qquad (2)$$

$$UO_2 + 2K_2S_2O_7 \rightarrow K_4U(SO_4)_4 \qquad (3)$$

The peak at 550°C was due to the decomposition of $K_4U(SO_4)_4$ to give $K_4UO_2(SO_4)_3$.

The TG curve of the reaction mixture of UO_2 with $2K_2S_2O_7$ showed mass loss only in a single step between 415°C and 650°C. As expected, the DTA curve of the mixture was identical to that of the reaction mixture of UO_2 and $K_2S_2O_8$, except for the exothermic peak at 205°C due to the decomposition of $K_2S_2O_8$ to $K_2S_2O_7$. The products formed at 400°C and 600°C were identified as $K_4U(SO_4)_4$ and $K_4UO_2(SO_4)_3$, respectively.

Table 1
Reaction products of UO_2, ThO_2 and mixed oxide $(U_x, Th_{1-x})O_2$ (where $x = 0.05$, 0.25 and 0.50) with $KHSO_4$ and $K_2S_2O_8$

Reactants	Temp. range (°C)	Mass loss (%)		Products identified[a]
		Obs.	Calc.	
$UO_2 + 4KHSO_4$	200–325	4.59	4.42	$K_4U(SO_4)_4$
	440–650	12.17	12.28	$K_4UO_2(SO_4)_3$
	900	–	–	$K_4UO_2(SO_4)_3 + K_2U_2O_7 + K_2O$
$UO_2 + 2K_2S_2O_8$	200–290	4.03	3.95	$K_4U(SO_4)_4$
	450–640	11.56	11.92	$K_4UO_2(SO_4)_3$
	900	–	–	$K_4UO_2(SO_4)_3 + K_2U_2O_7 + K_2O$
$ThO_2 + 4KHSO_4$	200–350	4.27	4.42	$K_4Th(SO_4)_4$
	600	–	–	$K_4Th(SO_4)_4$
	900	–	–	$K_2SO_4 + ThO_2$
$ThO_2 + 2K_2S_2O_8$	200–280	3.98	3.98	$K_4Th(SO_4)_4$
	600	–	–	$K_4Th(SO_4)_4$
	900	–	–	$K_2SO_4 + ThO_2$
$(U_x, Th_{1-x})O_2 + 4KHSO_4$	400	–	–	$K_4(U, Th)(SO_4)_4$
	600	–	–	$K_4(U, Th)O_2(SO_4)_3$
	900	–	–	$K_2U_2O_7 + ThO_2 + K_2SO_4$

[a] Products identified by XRD and/or thermogravimetry.

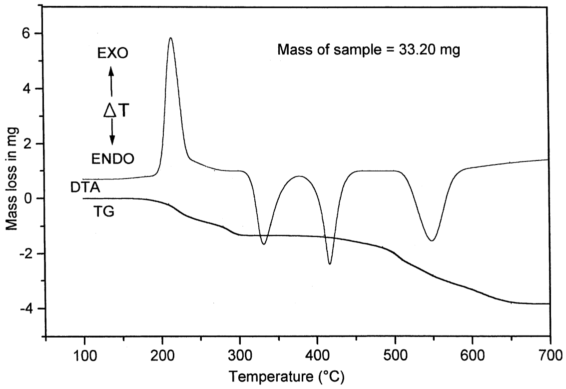

Fig. 2. TG and DTA curves of $UO_2 + 2K_2S_2O_8$.

After heating at 900°C for 4 h, the products were identified as mixtures of $K_4UO_2(SO_4)_3 + K_2U_2O_7 + K_2O$ (Table 1) from their XRD patterns.

3.3. Reactions of ThO_2 and $(U_x, Th_{1-x})O_2$ with $KHSO_4$, $K_2S_2O_8$ and $K_2S_2O_7$

Thermograms of a reaction mixture of ThO_2 with $KHSO_4$ and $K_2S_2O_8$ in a Th to K ratio of 1:4 are given in Figs. 3 and 4, respectively. In the TG curve of the mixture of ThO_2 and $KHSO_4$, the mass loss was observed in the range 200–350°C. The DTA curve showed only one endothermic peak at 225°C, due to the combined effect of melting of $KHSO_4$ and its reaction with ThO_2. In the TG curve of the reaction mixture of ThO_2 and $2K_2S_2O_8$, the mass loss was observed between 200°C and 280°C, due to the conversion of $K_2S_2O_8$ to $K_2S_2O_7$. The DTA curve of the mixture showed exothermic peak at 210°C and two endothermic peaks at 335°C and 405°C, similar to those observed in the DTA curve of the reaction mixture of UO_2 and $2K_2S_2O_8$ up to 500°C. The thermogram of the reaction mixture of ThO_2 with $2K_2S_2O_7$, showed no mass loss up to 700°C. As expected, the DTA curve of the mixture was identical to that of the reaction mixture of ThO_2 with $2K_2S_2O_8$, except for the exothermic peak at 210°C. At 400°C, the product formed during the reactions of ThO_2 with $KHSO_4, K_2S_2O_8$ and $K_2S_2O_7$ was identified as $K_4Th(SO_4)_4$, by mass loss and XRD. $K_4Th(SO_4)_4$ was observed to be stable up to 700°C, beyond which it decomposed to form K_2SO_4 and ThO_2. Various products formed during the reaction of ThO_2 with potassium salts are given in Table 1. The XRD data of $K_4Th(SO_4)_4$ was indexed on the triclinic system with the cell parameters given in Table 2. The similarities in the cell parameters of $K_4U(SO_4)_4, K_4Th(SO_4)_4$ and $(NH_4)_4U(SO_4)_4$ [7] suggest all three compounds are isostructural. The indexed X-ray data of $K_4Th(SO_4)_4$ are given in Table 3.

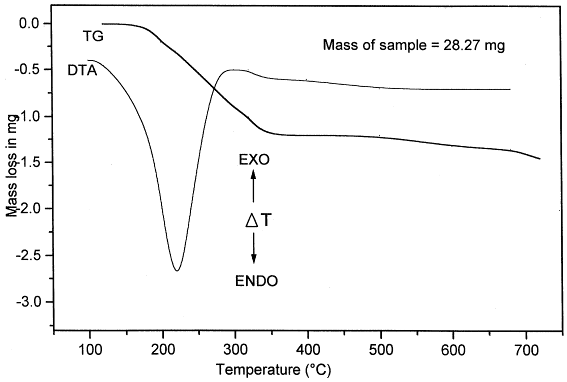

Fig. 3. TG and DTA curves of $ThO_2 + 4KHSO_4$.

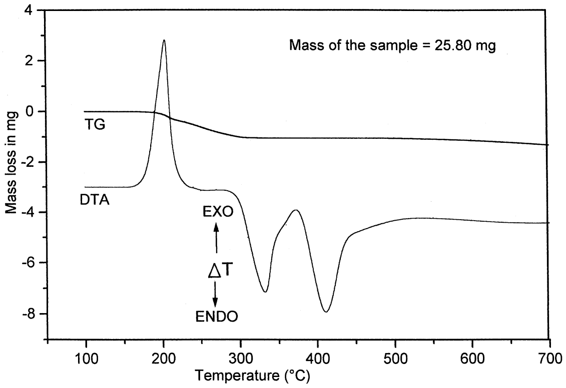

Fig. 4. TG and DTA curves of $ThO_2 + 2K_2S_2O_8$.

The mixed oxides of $(U_x, Th_{1-x})O_2$ with $x = 0.05$, 0.25 and 0.50 were reacted for 6–8 h with all the three potassium salts at various temperatures. At 400°C, the mixed oxides formed double sulphates of composition $K_4(U_x, Th_{1-x})(SO_4)_4$. XRD patterns of the products, obtained by heating the various mixed oxides of uranium and thorium, were similar to those of $K_4U(SO_4)_4$ and $K_4Th(SO_4)_4$. On heating $K_4(U_x, Th_{1-x})(SO_4)_4$ at 600°C, the products were identified as a mixture of $K_4UO_2(SO_4)_3$ and $K_4Th(SO_4)_4$. Further heating at 900°C, led to the formation of a mixture of $K_2SO_4, K_2U_2O_7$ and ThO_2. All the compounds formed during these reactions are included in Table 1.

4. Dissolution and separation studies

In order to study the quantitative dissolution of oxides, weighed amounts of UO_2, ThO_2 and $(U_x, Th_{1-x})O_2$ were mixed separately with $KHSO_4$ and heated in the furnace at 400°C for 6–8 h. All the products were treated with warm 2 M HNO_3 and solutions were analysed for uranium and thorium content. Uranium was analysed

Table 3
XRD data of $K_4Th(SO_4)_4$, $\lambda = 0.15406$ nm

h	k	1	$d_{\text{obs.}}$ (nm)	$d_{\text{calc.}}$ (nm)	I/I_0
−1	0	1	0.9522	0.9520	100
1	0	1	0.7570	0.7552	93
−2	−1	2	0.6468	0.6475	77
2	−1	0	0.5460	0.5455	70
−1	−2	1	0.4350	0.4354	50
−3	0	2	0.4279	0.4280	63
−2	−2	1	0.4070	0.4073	37
1	−2	0	0.3419	0.3420	41
1	2	0	0.3397	0.3396	59
−4	−2	1	0.3234	0.3234	52
−3	−1	4	0.3093	0.3096	10
1	−3	3	0.3027	0.3026	76
1	−3	2	0.2964	0.2963	68
−4	−3	4	0.2926	0.2926	< 5
0	−3	1	0.2726	0.2726	37
−6	−3	4	0.2498	0.2497	32
−1	−4	3	0.2396	0.2396	28
7	0	1	0.2239	0.2239	9
−6	−1	5	0.2154	0.2154	32
5	−3	3	0.2104	0.2105	< 5
7	0	2	0.1980	0.1981	31
−7	1	4	0.1687	0.1687	28

Table 4
Dissolution data of the products formed by reacting UO_2, ThO_2 and mixed oxides of $(U, Th)O_2$ with potassium salts

Oxides	Metal content in mixed oxide (mg)		% of metal dissolved	
	U	Th	U	Th
UO_2	500	–	97.3	–
ThO_2	–	500	–	98.1
$(U_{0.25}, Th_{0.75})O_2$	125	375	95.4	93.7
$(U_{0.50}, Th_{0.50})O_2$	250	250	93.2	92.8
$(U_{0.05}, Th_{0.95})O_2$	25	475	92.7	65.0

by chemical analysis using redox titrimetric method. The thorium content in the products obtained by reacting thorium oxide with $KHSO_4$ was determined by EDTA titrimetric method using xylenol orange as indicator. As uranium interferes here, dissolved thorium content in the solution was analysed by precipitating it as thorium oxalate with oxalic acid [14]. Results of the analysis of uranium and thorium content in the dissolved products are given in Table 4, which show that most of the oxide could be brought into soluble form by reacting with the sulphates of potassium used in this study.

Separation of uranium and thorium from the dissolved mixed oxide solution in HNO_3 was attempted by the precipitation method using oxalic acid [14]. The solution was heated to 70°C and 10% oxalic acid in water was slowly added with constant stirring. After allowing to settle for 1–2 h, the precipitate was filtered and heated to 750°C for its conversion to oxide and weighed as ThO_2. It was observed that during the precipitation thorium separated selectively as thorium oxalate whereas uranium did not precipitate with oxalic acid from the solution of mixed oxide. About 94% of thorium was recovered by oxalic acid precipitation and about 90% uranium was recovered as U_3O_8 from the solution by the ammonium diuranate (ADU) route. These studies suggest that reactions of potassium salts with mixed oxides of uranium and thorium can be used for the quantitative dissolution and separation of uranium and thorium from mixed oxides.

5. Conclusion

UO_2, ThO_2 and their mixed oxides (heat treated up to 1200°C) react at 400°C with sulphates of potassium to form $K_4U(SO_4)_4, K_4Th(SO_4)_4$ and $K_4(U, Th)(SO_4)_4$, respectively. XRD data of these compounds were indexed on the triclinic crystal system. The products formed by heating all the oxides with potassium salts up to 900°C were soluble in 2 M HNO_3. Uranium and thorium in the dissolved solution of the products formed during the reaction of mixed oxides with the sulphates were separated selectively by precipitating thorium with oxalic acid.

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