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Preparation, characterization and thermal stability of tellurites and tellurates of uranium

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Uranium tellurates, $UTeO_5$ and UTe_3O_9 were prepared by heating $UO_2 + TeO_2$ and $U_3O_8 + TeO_2$ in air/oxygen and the tellurite UTe_3O_8 by heating $UO_2 + TeO_2$ in vacuum sealed quartz ampoule. The compounds were characterized by X-ray diffraction (XRD) and thermogravimetry (TG). A new tellurite compound $UTeO_4$ was synthesized. Their thermal stability was determined in oxygen, argon and argon-8%hydrogen in the temperature range of ambient temperature to 950 °C. $UTeO_5$ and UTe_3O_9 are stable in flowing oxygen up to 925 and 750 °C, respectively under dynamic heating at 10 K/min. UTe_3O_9 decomposes in O_2/Ar/Ar-8%H_2 via formation of $UTeO_5$, whereas UTe_3O_8 decomposes in Ar-8%H_2 via formation of $UTeO_4$. UTe_3O_9 decomposes at 560 °C but all the other compounds decompose at 460 °C in Ar-8%H_2. *© 2000 Kluwer Academic Publishers*

1. Introduction

Three ternary compounds in the UO_{2+x}-TeO_2-O section of the U-Te-O system namely, $UTeO_5$, UTe_3O_8 and UTe_3O_9 are reported in the literature. $UTeO_5$ and UTe_3O_8 are known as schmidtterite and cliffordite respectively. Most of the reported work on synthesis of uranium tellurates: $UTeO_5$ and UTe_3O_9 is confined to solution route. $UTeO_5$ was initially prepared [1] by the reaction of uranyl acetate with hydrochloric acid solution of TeO_2 at room temperature. Later, $UTeO_5$ [2] and UTe_3O_9 [3] were prepared by high pressure synthesis in vycor tubes in stainless steel bomb by heating water solutions of the mixtures: $UO_3{\cdot}H_2O + TeO_2$ and $UF_4 + TeO_2 + H_2O_2$ in the temperature range of 100–400 °C. There is only one report [4] on the solid state synthesis of these compounds in sealed vycor tubes from the mixtures: $UO_3 + TeO_2$ and $UO_2 + TeO_2$ at 700 °C. There is no systematic study on solid state preparation of the compounds from UO_2 and U_3O_8 in O_2/air and their thermal stability. In addition, the existence of UTe_3O_8 is suspect in view of the reaction: $4UO_2 + 12TeO_2 \rightarrow UTeO_5 + 3UTe_3O_9 + 2Te(g)$ reported in [4]. The present work is undertaken in order to address the questions of synthesis, existence and stability of the tellurites and tellurates in general and, $UTeO_4$ and UTe_3O_8 in particular. The studies are of utmost importance and interest in assessing the possibility of formation of these compounds in irradiated UO_2 based nuclear fuels.

2. Experimental

The two main experimental techniques used in this work were thermogravimetry (TG) and differential thermal analysis (DTA). In addition, X-ray diffractometry (XRD) was employed for the identification of various condensed phases.

2.1. Materials

TeO_2 is 99.995% pure (Aldrich). UO_2 was prepared from nuclear pure UO_{2+x} (supplied by Atomic Fuels Division, BARC) by reduction in Ar-8%H_2 stream. U_3O_8 was obtained by heating the UO_{2+x} sample at 700 °C in oxygen to a constant mass.

2.2. X-ray diffraction (XRD)

Phase characterization of the starting materials e.g. UO_2, U_3O_8 and TeO_2 and the compounds prepared was carried out by XRD at ambient temperature using the Philips X-ray powder diffractometer (Model No. P.W. 1729/40) with nickel filter and graphite monochromator.

2.3. Thermogravimetry (TG)

The initiation temperatures and steps in various compound formation reactions from the mixtures: $UO_2 + TeO_2$ and $U_3O_8 + TeO_2$ in flowing oxygen were recorded at a heating rate of 10 K/min on a thermogravimetric balance (Model Shimatzu DT-30) at a sensitivity of $\pm 50\ \mu g$. The TG balance was also employed for determinations of the oxygen stoichiometry of the reactants and the products.

The thermocouple of the TG apparatus and the chart temperature were calibrated by employing drop method described in [5]. The sudden change in mass resulting due to drop of indium, Te, Sb, silver and pellet of Li_2SO_4 on melting was registered at 157, 449.5, 630.6,

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859 and 961.8 °C respectively. The above pure substances were suspended freely by a thin steel wire from the central suspension wire of the thermogravimetric balance.

2.4. Differential thermal analysis (DTA)

DTA was carried out employing a home made and upgraded DTA unit [6] in flowing argon. The melting points of $UTeO_4$ and UTe_3O_8 were determined by DTA. The DTA apparatus was calibrated with melting points of Zn (419.5 °C), Te (449.5 °C), TeO_2 (733 °C) and Ag (961.8 °C). The calibrants and the compounds investigated were all contained in silica DTA crucibles. The crucibles were sealed under vacuum ($\sim 10^{-4}$ Torr).

2.5. Preparation and characterization of the compounds

$UO_{2.00}$ was prepared by heating UO_{2+x} in Ar-8%H_2 stream at 750 °C while U_3O_8 was prepared by heating in oxygen stream at 700 °C.

$UTeO_5$ and UTe_3O_9 were prepared by heating (1 : 1) and (1 : 3) mixtures of UO_2 and TeO_2 in oxygen at 600 °C first for 4 h and then at 720 °C for 2 h. The formation of these compounds can be represented by the following reactions;

$$UO_{2.00}(s) + TeO_2(s) + \frac{1}{2}O_2(g) = UTeO_5(s) \quad (F1)$$

and

$$UO_{2.00}(s) + 3TeO_2(s) + \frac{1}{2}O_2(g) = UTe_3O_9(s) \quad (F2)$$

These compounds were also prepared by an alternate route using U_3O_8 according to the reactions given below:

$$U_3O_8(s) + 3TeO_2(s) + \frac{1}{2}O_2(g) = 3UTeO_5(s) \quad (F3)$$

and

$$U_3O_8(s) + 9TeO_2(s) + \frac{1}{2}O_2(g) = 3UTe_3O_9(s) \quad (F4)$$

by heating the mixtures of U_3O_8 and TeO_2 in (1 : 3) and (1 : 9) proportions at 650 °C for 3 h.

Thermogravimetric study of the synthesis of the above compounds in dynamic heating at the rate of 10 K/min shows attainment of constant mass hence completion of the formation reaction at 690 °C. The results are presented in Table I and Fig. 2.

$UTeO_4$ and UTe_3O_8 were prepared by mixing requisite amounts of $UO_{2.00}$ and TeO_2 and heating at 450 and 750 °C, respectively in silica ampoules sealed under vacuum according to the reactions below:

$$UO_2(s) + TeO_2(s) = UTeO_4(s) \quad (F5)$$

and

$$UO_2(s) + 3TeO_2(s) = UTe_3O_8(s) \quad (F6)$$

All the above compounds thus synthesized were characterized thermogravimetrically for their oxygen contents by dynamic heating in oxygen and/or argon and phase analysed by XRD. The results are given in Table II. $UTeO_4$ being reported for the first time does not have any standard powder pattern to compare with.

The X-ray powder patterns of $UTeO_4$ and UTe_3O_8 had lines different from those of UO_2 and TeO_2 (Fig. 1)

TABLE I Thermogravimetric results of synthesis

Mixture	Temperature range (°C)	Environment	Initial mass (mg)	Constant mass (mg)	Calculated mass of compound (mg)	Stoichioimetry	Phase (XRD)
$UO_{2.00} + TeO_2$	380–700	flo.O_2	63.65	66.05	66.02	$UTeO_{5.01}$	$UTeO_5$
$UO_{2.00} + 3TeO_2$	350–700	-do-	110.90	113.30	113.27	$UTe_3O_{9.01}$	UTe_3O_9
$U_3O_8 + 3TeO_2$	510–700	-do-	48.90	49.54	49.49	$UTeO_{5.03}$	$UTeO_5$
$U_3O_8 + 9TeO_2$	510–710	-do-	53.80	54.18	54.18	$UTe_3O_{9.00}$	UTe_3O_9

TABLE II Results of thermogravimetric characterization of the compounds

Compound	Temperature range (°C)	Environment	Initial mass (mg)	Constant mass (mg)	Stoichiometry	Phase (XRD)
$UO_{2.00}$	150–240	flo. O_2	48.05	49.00	$U_3O_{7.007}$	U_3O_7
	330–370	-do-	49.00	49.95	$U_3O_{8.01}$	U_3O_8
$U_3O_{8.01}$	485–700	Ar-8%H_2	49.95	48.04	$UO_{2.00}$	UO_2
TeO_2	R.T-575	flo. Ar	12.00	12.00	$TeO_{2.00}$	TeO_2
	R.T.-575	flo. O_2	10.30	10.30	$TeO_{2.00}$	TeO_2
$UTeO_{5.01}$	R.T.-930	flo. O_2	40.00	40.00	$UTeO_{5.01}$	$UTeO_5$
	R.T.-900	flo. Ar	10.00	10.00	$UTeO_{5.01}$	$UTeO_5$
$UTe_3O_{8.00}$	R.T.-700	flo. O_2	10.00	10.22	$UTe_3O_{9.01}$	UTe_3O_9
$UTe_3O_{9.01}$	R.T.-750	flo. O_2	40.00	40.00	$UTe_3O_{9.01}$	UTe_3O_9
	R.T.-750	flo. Ar	40.00	40.00	$UTe_3O_{9.01}$	UTe_3O_9
$UTeO_{4.00}$	R.T.-750	flo. O_2	11.50	11.94	$UTeO_{5.05}$	$UTeO_5$

flo. = flowing, R.T. = room temperature.

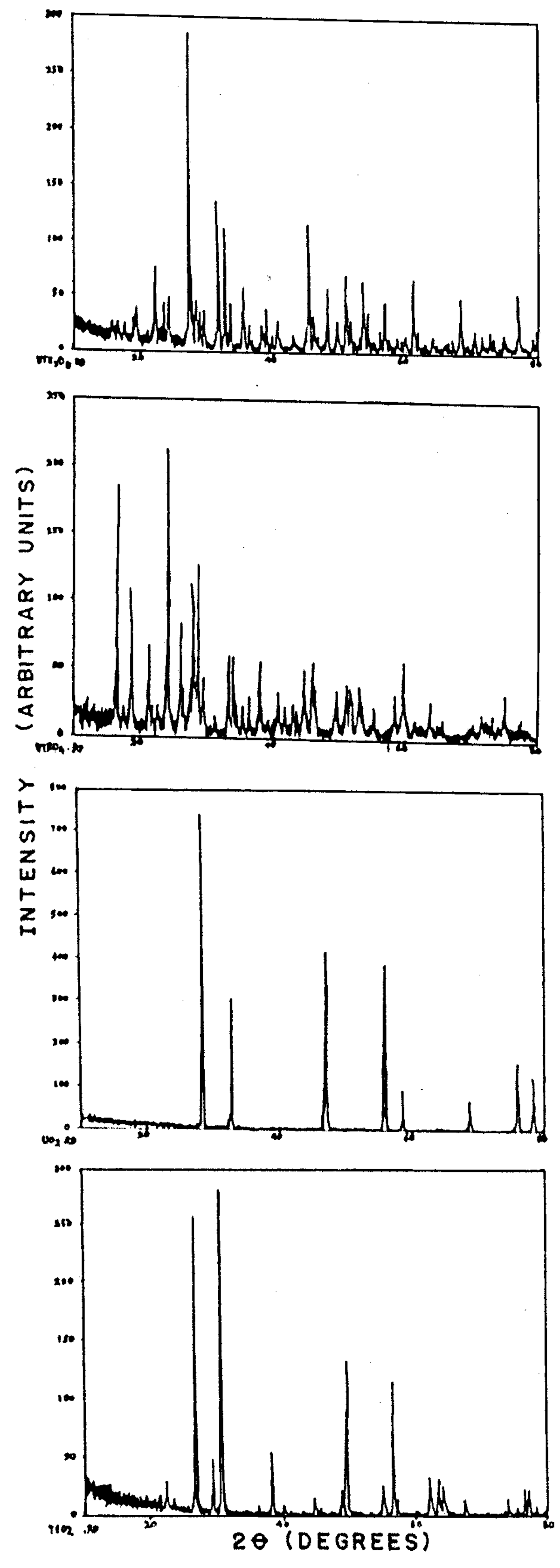

Figure 1 XRD patterns of TeO_2, UO_2, $UTeO_4$ and UTe_3O_8.

and the lines characteristic of UO_2 and TeO_2 were absent. The patterns were noticeably different from those of the corresponding mechanical mixtures of the two constituents. In addition, these phases melted at 1100 and 855 °C, respectively which are different from the melting points of the constituents: UO_2 (2865 °C) and TeO_2 (733 °C). The XRD and melting point evidences confirm that the above substances are compounds and not mixtures of UO_2 and TeO_2.

Thermal stabilities of all the above compounds were studied in the temperature range of ambient temperature—950 °C by thermogravimetry in flowing oxygen, argon and Ar-8%H_2. The composition of the compounds were determined by complete decomposition to constant mass in argon, oxygen and Ar-8%H2 streams. The results are presented in Tables III and IV.

3. Results and Discussion

The reactions (F1), (F2), (F3) and (F4) involve intake of oxygen. Uranium dioxide is known to take up oxygen in solid solution to varying extents. Hence it was considered imperative to accurately determine the oxygen contents of the condensed phases and define the chemical reactions precisely. Therefore, oxygen stoichiometries of the reactants: UO_2, U_3O_8, TeO_2 and the products: $UTeO_4$, $UTeO_5$, UTe_3O_8 and UTe_3O_9 were determined by TG in oxygen and argon. The results are presented in Table II.

The starting material uranium dioxide obtained by reduction of UO_{2+x} in Ar-8%H_2 at 750 °C and physically characterized by XRD as UO_2, was thermogravimetrically characterized for oxygen stoichiometry by dynamic heating at 10 K/min in flowing oxygen. The oxidation took place in two steps; one in the range of 150–240 °C and the other in 330–370 °C leading to constant masses over 240–330 °C and 370–750 °C (Fig. 2a). The mass gain in 48.05 mg of UO_2 in each step of oxidation being equal to 0.8 mg, the end phases of the two steps were identified as U_3O_7 and U_3O_8. The oxygen stoichiometries of the two oxides calculated from the mass gain and the starting material being $UO_{2.00}$, worked out as $U_3O_{7.007}$ and $U_3O_{8.01}$ (Table II). The equality of the mass gains in the two steps, mass constancies corresponding to U_3O_7 and U_3O_8 and the calculated stoichiometries agreeing very closely to U_3O_7 and U_3O_8 confirm the oxygen stoichiometry of the reduced uranium dioxide as $UO_{2.00}$. The oxygen stoichiometry of the reduced uranium dioxide was further confirmed by thermogravimetric reduction of the above formed $U_3O_{8.01}$ in Ar-8%H_2 at 700 °C. 49.95 mg of $U_3O_{8.01}$ lost a part of its oxygen and attained constant mass of 48.04 mg corresponding to $UO_{2.00}$.

Similarly, TeO_2 containing 99.995% tellurium (IV) oxide and characterized by XRD, was thermogravimetrically analysed for oxygen content by heating in oxygen and argon streams upto 575 °C, wherein 10.30 and 12.00 mg of the substance run in oxygen and argon respectively did not gain or lose mass confirming the oxygen stoichiometry in tellurium dioxide as $TeO_{2.00}$.

Thus having experimentally established the oxygen stoichiometries of the reacting oxides as $UO_{2.00}$. $U_3O_{8.00}$ and $TeO_{2.00}$, the formation reactions $UTeO_5$ and UTe_3O_9 were thermogravimetrically investigated.

The (1 : 1) mixture of UO_2 and TeO_2 (63.65 mg) and the (1 : 3) mixture of U_3O_8 and TeO_2 (48.90 mg) heated dynamically in oxygen stream reacted with oxygen and attained constant mass of 66.05 and 49.54 mg respectively, remaining unchanged upto 700 °C. The mixture containing UO_2 undergoes reaction in two steps and

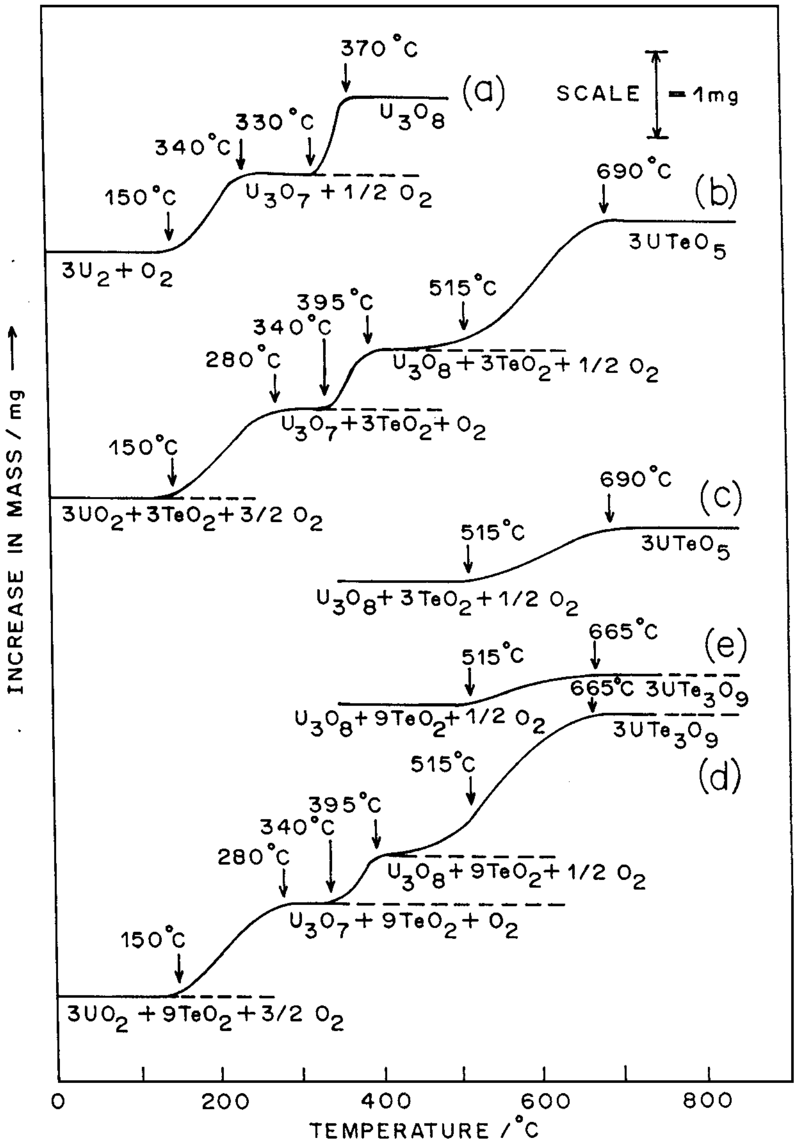

Figure 2 TG patterns of synthesis.

the one with U_3O_8 reacts only in one step as shown in Fig. 2b and c respectively and the reactions can be represented as:

$$3UO_2 + 3TeO_2 + \frac{3}{2}O_2 \rightarrow U_3O_7 + 3TeO_2 + O_2$$

$$\rightarrow U_3O_8 + 3TeO_2 + \frac{1}{2}O_2 \rightarrow UTeO_5 \qquad (a)$$

and

$$U_3O_8 + 3TeO_2 + \frac{1}{2}O_2 \rightarrow 3UTeO_5 \qquad (b)$$

The end products of the two routes calculated on the basis of mass gain work out to be $UTeO_{5.01}$ and $UTeO_{5.03}$ respectively. In case of $UO_2 + TeO_2$, the reaction of formation of $UTeO_5$ starts at 395 °C while in $U_3O_8 + TeO_2$ it begins at 515 °C, the temperature of initiation of formation of $UTeO_5$ in the former reaction being lower than that in the latter. The two mixtures prepared from the same batch samples of UO_2 and TeO_2 had nearly identical masses in the range of 50–60 mg with nearly equal exposed surface area (spread over 8 mm dia area in a quartz crucible). The origin, nature, size of particles and impurities present in the starting materials being nearly the same in the two, the diffusion barrier, if any, would be identical in the two cases. Hence the difference of 120 °C between the initiation temperatures of the two reactions is real and is most likely related to the reactivity of the *in-situ* generated U_3O_8. The inertness of the pure uranium oxides (prepared independently) at low temperatures is well known in the literature [7].

The reactivity of the *in-situ* generated U_3O_8 is inferred from the comparison of the thermograms b and c of the Fig. 2 recorded at one and the same heating rate (10 K/min). From b one can see that the formation of U_3O_8 begins at 340 °C and is complete by 395 °C, the initiation temperature of formation of $UTeO_5$ i.e. U_3O_8 remains in contact with TeO_2 only for ~6 min before entering into reaction to form $UTeO_5$ whereas from c it is amply clear that the period of contact between U_3O_8 and TeO_2 before the initiation of the reaction is ~52 min. Shorter contact period initiating a reaction at lower temperature vis-a-vis prolonged contact leading to the same reaction at a relatively higher temperature can only be understood in terms of the reactivity of the U_3O_8 powders in the two cases.

TABLE III Results of thermogravimetric decomposition of the compounds

Compounds	Temperature (°C)	Environment	Initial mass (mg)	Loss (mg)	Constant mass (mg)	Calculated ultimate mass (mg)	Residual phase	Remarks
$UTeO_5$	≥925	flo. O_2	10.00	3.15	—	—	$U_3O_8 + UTeO_5$	Partial Decomp.
	≥900	flo. Ar	10.00	3.75	6.25	6.30	U_3O_8	Compl. Decomp.
UTe_3O_9	≥750	flo. O_2	10.00	2.50	—	—-	$UTeO_5 + UTe_3O_9$	Partial Decomp.
	≥750	flo. Ar	10.00	6.35	3.65	3.67	U_3O_8	Compl. Decomp.

decomp. = decomposition, compl. = complete.

TABLE IV Results of thermogravimetric reduction in Ar-8%H_2

Compound	Temperature range (°C)	Initial mass (mg)	Residue mass (mg)	Calculated residue mass (mg)	Residual phase
$UTeO_4$	458–698	10.00	6.28	6.29	UO_2
$UTeO_5$	468–783	10.00	6.10	6.06	UO_2
UTe_3O_8	480–696	10.00	5.74	5.74	$UTeO_4$
	760–808	5.74	3.62	3.61	UO_2
UTe_3O_9	560–740	10.00	5.82	5.83	$UTeO_5$
	750–763	5.82	3.53	3.53	UO_2

The (1 : 3) mixture of UO_2 and TeO_2 (110.90 mg) and the (1 : 9) mixture of U_3O_8 and TeO_2 (53.80 mg) heated dynamically upto 700 °C in flowing oxygen in TG unit gained oxygen and saturated at constant mass of 112.90 and 54.18 mg respectively, leading to oxygen stoichiometries of $UTe_3O_{9.01}$ and $UTe_3O_{9.03}$. The steps in the thermogravimetric run shown in d and e in Fig. 2 are represented as:

$$3UO_2 + 9TeO_2 + \frac{3}{2}O_2 \rightarrow U_3O_7 + 9TeO_2 + O_2$$

$$\rightarrow U_3O_8 + 9TeO_2 + \frac{1}{2}O_2 \rightarrow 3UTe_3O_9 \qquad \text{(c)}$$

and

$$U_3O_8 + 9TeO_2 + \frac{1}{2}O_2 \rightarrow 3UTe_3O_9 \qquad \text{(d)}$$

Here too, the reaction initiation temperatures for the two mixtures being 395 and 515 °C and in the same sequence as observed in the synthesis of $UTeO_5$ represented by equations (a) and (b) endorse the higher activity of the *in situ* generated U_3O_8.

The compounds, $UTeO_4$ and UTe_3O_8, prepared from the (1 : 1) and (1 : 3) mixtures of UO_2 and TeO_2 by heating in vacuum sealed ampoules, have their melting points at 1100 and 855 °C, that are far different from those of the constituents; UO_2 (2830 °C) and TeO_2 (733 °C). Their inherent oxygen stoichiometry of UO_2 and TeO_2, mixed in the definite proportions of (1 : 1) and (1 : 3), fixes the composition of the resulting compounds to be $UTeO_4$ and UTe_3O_8. The powder diffraction pattern of UTe_3O_8 was observed to be identical to that of UTe_3O_9 as reported [4], whereas the pattern of $UTeO_4$ was by and large identical with that of $UTeO_5$ and had some additional diffraction lines. The unit cell of $UTeO_4$ is orthorhombic and has the dimensions: $a = 6.16$ Å, $b = 10.77$ Å and $c = 14.73$ Å. Since diffraction patterns are very closely similar for $UTeO_4$ and $UTeO_5$, the space group of $UTeO_4$ is likely to be $Pbc2_1$ or Pbcm i.e. the same as that of $UTeO_5$.

Thermogravimetric characterization of $UTeO_4$ was carried out by dynamic heating of the compound in flowing oxygen. 11.5 mg of the compound gained in oxygen to a constant mass of 11.95 mg (Table II) corresponding to $UTeO_{5.05}$. The mass gain equivalent to 0.5 mole of O_2 is consistent with the reaction;

$$UTeO_4(s) + \frac{1}{2}O_2(g) = UTeO_5(s)$$

The Oxygen stoichiometry of the synthesized product, $UTeO_{5.01}$, was characterized by thermogravimetry in oxygen and argon upto 885 °C in dynamic heating at 10 K/min. The initial mass of the compound remained unchanged indicating no gain or loss of oxygen. Thus the compound is characterized to be $UTeO_5$.

UTe_3O_8 was characterized by its reaction with oxygen, in which one mole of the compound would acquire one half of a mole of O_2 to form UTe_3O_9. In fact, 10 mg of the compound reacted with O_2 attained a constant mass of 10.22 mg leading to $UTe_3O_{9.03}$ which was phase characterized as UTe_3O_9 by XRD.

In characterization of UTe_3O_9 for its oxygen content by dynamic heating in oxygen as well as argon stream, 40 mg of the compound exhibited no mass change and remained stable upto 750 °C, confirming that the stoichiometry remained unchanged (Table II).

$UTeO_5$ heated dynamically in argon ($p_{O_2} \approx 4{\cdot}10^{-6}$ atm) in 10 mg quantity starts decomposing above 900 °C and continues to lose till constant mass and yields a residue of 6.25 mg corresponding to U_3O_8 (Fig. 3b). $UTeO_5$ in dynamic heating in oxygen stream decomposes above 925 °C (Fig. 3a). The partially decomposed substance contained U_3O_8 and $UTeO_5$ phases as analysed by XRD. The higher initiation temperature of decomposition of $UTeO_5$ in oxygen compared to that in argon supports the evolution of O_2 in the decomposition process. Hence the decomposition of $UTeO_5$ can be represented by the reaction:

$$3UTeO_5(s) \rightarrow U_3O_8(s) + 3TeO_2(g) + \frac{1}{2}O_2(g) \qquad \text{(D1)}$$

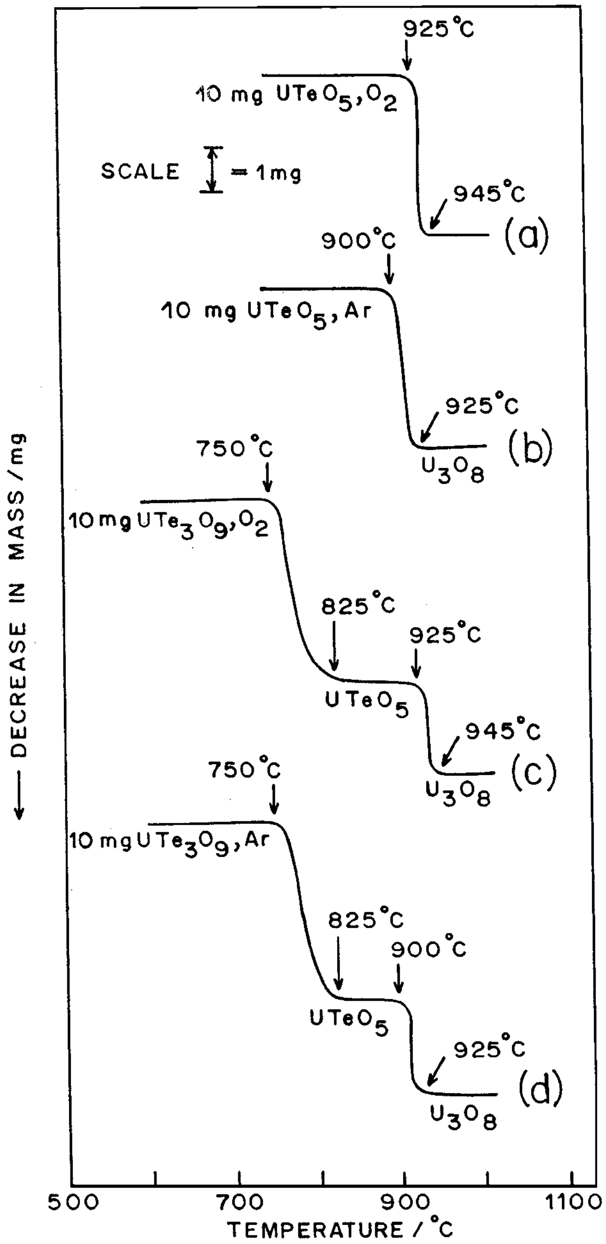

Figure 3 Thermal decomposition in O_2/Ar.

UTe_3O_9 heated dynamically in TG in oxygen or argon stream begins decomposing at 750 °C very slowly and above 900 °C the decomposition is quite fast and complete (Fig. 3c and d) leading to constant mass residue of 3.65 mg in 10 mg sample. The residue is characterized as U_3O_8 by XRD. Thus the complete decomposition can be shown by the reaction;

$$3UTe_3O_9(s) \rightarrow U_3O_8(s) + 9TeO_2(g) + \frac{1}{2}O_2(g) \quad (D2)$$

The partial decomposition at 750 °C occurs via formation of $UTeO_5$ and the process can be written as:

$$UTe_3O_9(s) \rightarrow UTeO_5(s) + 2TeO_2(g) \quad (D3)$$

The same initiation temperature of 750 °C in flowing O_2 and Ar for the thermogravimetric decomposition of UTe_3O_9 proves that O_2 has no role in the process and establishes that (D3) is the true representation of the decomposition.

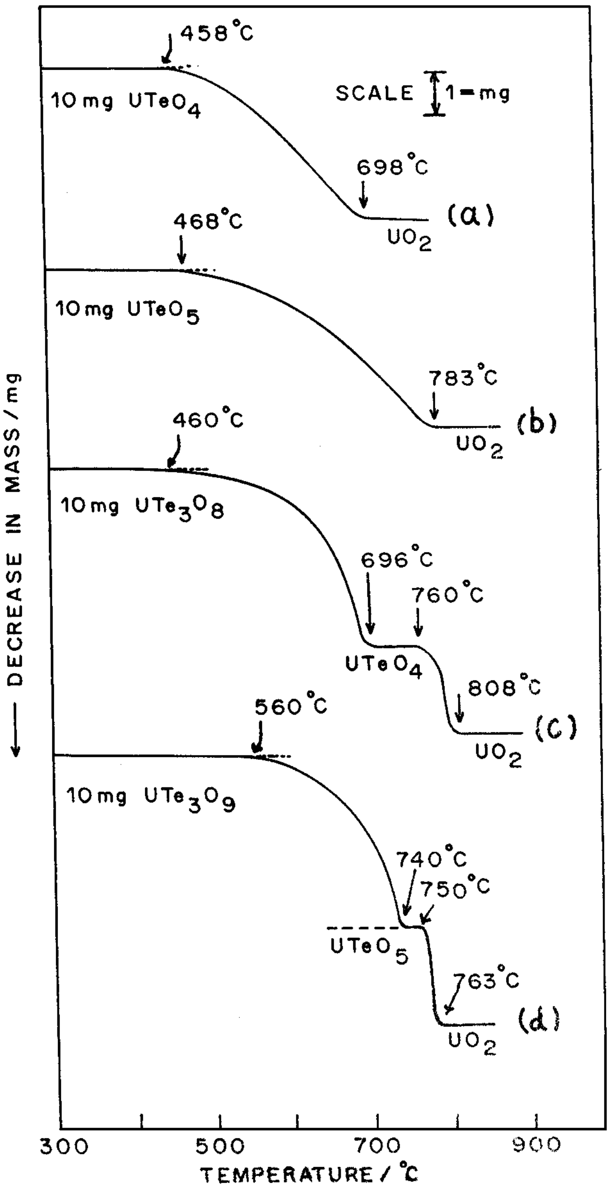

Figure 4 Thermal decomposition in Ar-8%H_2.

The decomposition reactions (D1) and (D2) shall form the basis of determining equilibrium pressure of TeO_2, p_{TeO_2}, over $U_3O_8 + UTeO_5$ and $U_3O_8 + UTe_3O_9$ at fixed O_2 pressure ($\sim$1 atm) by transpiration method and hence for the derivation of the Gibbs free energy of formation of $UTeO_5$ and UTe_3O_9 [8]. Similarly, the reaction (D3) can be used for transpiration in inert atmosphere and determination of the free energies of formation of UTe_3O_9.

3.1. Reductive decomposition in Ar-8%H_2

The results of thermogravimetric decomposition of $UTeO_4$, $UTeO_5$, UTe_3O_8 and UTe_3O_9 in Ar-8%H_2 under dynamic heating at 10 K/min are presented in Table IV and Fig. 4. In all these experiments metallic tellurium, identified by XRD, was observed downstream in the reaction tube implying that Te(g) was formed as a product in the reaction.

$UTeO_4$ prepared by heating the mixture of UO_2 and TeO_2 or by the thermal decomposition of UTe_3O_8 in Ar-8%H_2 decomposes in the range of 458–698 °C (Fig. 4a).

Initial mass of 10.00 mg of $UTeO_4$ yielded a constant mass residue of 6.28 mg corresponding to UO_2, as characterized by mass balance and XRD, establishing the decomposition reaction as:

$$UTeO_4(s) + 2H_2(g) \rightarrow UO_2(s) + Te(g) + 2H_2O(g) \quad \text{(R1)}$$

Similarly, $UTeO_5$ prepared by heating a mixture of UO_2 and TeO_2 in oxygen and also by decomposition of UTe_3O_9 in Ar-8%H_2 was observed decomposing in the temperature range of 468–783 °C and yielded a constant mass residue of 6.10 mg at 783 °C in an initial mass of 10.00 mg (Fig. 4b). The residue was identified as UO_2 by mass and phase analysis. The reaction involved can be written as:

$$UTeO_5(s) + 3H_2(g) \rightarrow UO_2(s) + Te(g) + 3H_2O(g) \quad \text{(R2)}$$

UTe_3O_8 and UTe_3O_9 undergo decomposition in two steps via the formation of the $UTeO_4$ and $UTeO_5$ respectively, as identified by XRD.

The I step in the decomposition of UTe_3O_8 occurs in the temperature range of 460–696 °C leading to a constant mass residue of 5.74 mg of $UTeO_4$ at 696 °C in a sample of 10.00 mg. Mass loss that occurs in reaching the I step of reductive decomposition of UTe_3O_8 corresponds to two moles of $TeO_2(g)$ and the residue has mass equivalent to that of $UTeO_4$. The residue was identified by XRD as $UTeO_4$ and the pattern matched with that of the compound initially prepared and characterized by comparison with those of UO_2 and TeO_2. Thus was established that the I step decomposition product of UTe_3O_8 in Ar-8%H_2 was $UTeO_4$ only. This residual $UTeO_4$ remains stable upto 760 °C and starts decomposing at higher temperatures giving rise to II step of decomposition of UTe_3O_8 and attains at 808 °C a constant mass of 3.62 mg in an initial mass of 5.74 mg of the I step residue (Fig. 4c). The final residue was characterized as UO_2 by mass balance and XRD. The decomposition of of the *in-situ* formed $UTeO_4$ in the single run decomposition of UTe_3O_8 occurs at a higher temperature (760 °C) compared to that (458 °C) of the independently prepared $UTeO_4$. When the decomposition run of UTe_3O_8 is stopped at complete conversion to $UTeO_4$ and the residue is cooled to room temperature and subjected to TG run, the decomposition begins at at 458 °C endorsing the stability of $UTeO_4$ upto 458 °C (Fig. 4a). The apparent anomaly of higher temperature of decomposition of of $UTeO_4$ in the TG run of UTe_3O_8 is explained to be due to higher moisture potential of UTe_3O_8 decomposition (equation R3) compared to that of $UTeO_4$ (equation R1). The decomposition behaviour of UTe_3O_8 can be represented by the following chemical reactions:

$$\begin{aligned} &UTe_3O_8(s) + 4H_2(g) \rightarrow UTeO_4(s) + 2Te(g) + 4H_2O(g) \\ &\qquad\qquad |{+2H_2} \\ &\qquad\qquad \rightarrow UO_2(s) + Te(g) + 2H_2O(g) \quad \text{(R3)} \end{aligned}$$

UTe_3O_9 starts decomposing at 560 °C yielding a mixture of $UTe_3O_9 + UTeO_5$. The decomposition to $UTeO_5$ is complete at 740 °C yielding a constant mass residue of 5.82 mg in 10.00 mg sample of UTe_3O_9 (Fig. 4d). The residual $UTeO_5$ (5.82 mg) undergoes decomposition at 750 °C and completes the process at 763 °C giving a constant mass residue of 3.53 mg characterized as UO_2. Here too, the decomposition of the *in-situ* formed $UTeO_5$ in the continuous run occurs at higher temperature (750 °C) than that (468 °C) of the independently prepared $UTeO_5$, the reason being the same as stated above. The decomposition of UTe_3O_9 can be expressed by the following reactions:

$$\begin{aligned} &UTe_3O_9(g) + 4H_2(g) \rightarrow UTeO_5(s) + 2Te(g) + 4H_2O(g) \\ &\qquad\qquad |{+4H_2} \\ &\qquad\qquad \rightarrow UO_2(s) + Te(g) + 3H_2O(g) \quad \text{(R4)} \end{aligned}$$

3.2. Possibility of formation in irradiated nuclear fuel UO_2

The reaction (F3) can be rewritten as;

$$UO_{2.67} + TeO_2 + 0.33/2O_2 = UTeO_5 \quad \text{(F3)}$$

Perusal of reactions (F1) and (F3) shows that presence of oxygen is essential for the formation of $UTeO_5$ from UO_2 as well as $UO_{2.67}$. Though $UO_{2.67}$ has a higher oxygen content than UO_2, yet it needs oxygen, of course a smaller quantity ($0.33/2O_2$), to form $UTeO_5$. In other words, oxygen potential for the formation of $UTeO_5$ is even higher than that of U_3O_8 and corresponds to that of UO_3. Similarly, (F4) rewritten as;

$$UO_{2.67} + 3TeO_2 + 0.33/2O_2 = UTe_3O_9 \quad \text{(F4)}$$

can be compared with (F2). The conclusion is that the formation of UTe_3O_9 also requires an oxygen potential higher than that of U_3O_8 and corresponding to that of UO_3. Thus it is established that an environment with oxygen potential higher than that of U_3O_8 and corresponding to that of UO_3 is essential for the formation of both of $UTeO_5$ and UTe_3O_9. As a matter of fact the oxygen potential in an operating nuclear fuel is lower than that of even $UO_{2.24}$, the oxygen-rich boundary of UO_{2+x} phase (at 1100 °C) [9] as required by fuel design. Hence, the formation of $UTeO_5$ and UTe_3O_9 in UO_2-based operating nuclear fuels is ruled out. Efforts are afoot to determine thermodynamic stabilities of $UTeO_4$ and UTe_3O_8.

4. Conclusions

In situ generated U_3O_8 is more reactive towards TeO_2 than independently prepared U_3O_8. The complete decomposition of the compounds $UTeO_4$, $UTeO_5$, UTe_3O_8, UTe_3O_9 can be employed as a method of determination of their compositions in terms of mol % of TeO_2.

$UTeO_4$ and UTe_3O_8 could form in UO_2-based operating nuclear fuel while there is no possibility of formation of $UTeO_5$ and UTe_3O_9 in a nuclear reactor except in an accident involving rush-in of air.

The reductive decomposition of $UTeO_4$, $UTeO_5$, UTe_3O_8 and UTe_8O_9 in Ar-8%H_2 gas occuring around 600 °C is quite rapid due to rapid vaporization of tellurium formed therein. Hence, the process can serve as another method of analysis of composition of the said compounds in terms of TeO_2.

$UTeO_5$ decomposes at a higher temperature than that for UTe_3O_9. The latter decomposes via formation of the former. Hence, $UTeO_5$ is more stable than UTe_3O_9.

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