Thermochimica Acta, 79 (1984) 377–382
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMOGRAVIMETRIC STUDY OF SOME URANIUM MOLYBDATES

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(Received 28 March 1984)

Thermodynamic data of uranium molybdates are necessary in understanding the chemical form of molybdenum present in high burn-up oxide nuclear fuels [1] as well as in the analysis of the molybdenum transport across such oxide pellets under temperature gradients. A research programme to obtain thermodynamic data of selected uranium molybdates was initiated recently in this laboratory and a partial ternary phase diagram of U–Mo–O has been described [2]. Four ternary oxide phases, namely $UMoO_5$, U_2MoO_8 UMo_2O_8 and $UMoO_6$, have been isolated and characterised in this ternary system. Results of a systematic study of their thermal stability using TG is presented in this report.

As the availability of pure, single phase samples of these mixed oxides was an essential a priori requirement for all subsequent investigations, special attention was paid to the preparative procedure for these uranium molybdates. When following previously reported methods of their preparation [3–8], involving heating the appropriate mixtures of the two binary oxides in sealed silica tubes, in proper stoichiometry, several times the pure, single phase ternary oxide could not be obtained. The relatively high volatility of $MoO_3(s)$ at the reaction temperatures could have been the cause of this. Hence, modified preparation procedures were adopted to synthesise pure, single phase samples of each of these four uranium molybdates.

In the preparation procedure, the loss of $MoO_3(s)$ due to vaporization altering the stoichiometry was circumvented by a stepwise synthesis of the desired compound. Thus, $UMoO_6$ was prepared by heating a mixture of UO_2 and MoO_3 in dry air. Initially at 410 K, UO_2 was oxidized to U_3O_7 followed by oxidation to U_3O_8 at 505 K. This in-situ generated U_3O_8 is very reactive and combines readily with MoO_3 forming $UMoO_6$ before the vaporization of $MoO_3(s)$ becomes appreciable. Thus, at 940 K the formation reaction was complete, and pure, single phase $UMoO_6$ was obtained. The mode of formation of $UMoO_6$ was established by TG [9]. This procedure contrasts with the previous method of heating U_3O_8 and MoO_3 directly in air at 1000 K which invariably results in a mixture of ($UMoO_6 + U_3O_8$).

TABLE 1

X-ray diffraction data: inter-planar spacings of $UMoO_5$, $UMoO_6$, UMo_2O_8 and U_2MoO_8

$UMoO_5$				$UMoO_6$				UMo_2O_8				U_2MoO_8			
This work		Ref. 4		This work		Ref. 8		This work		Ref. 4		This work		Ref. 5	
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
6.371	18	6.33	30	6.916	15	—	—	4.114	100	4.110	100	5.829	5	5.79	20
4.152	100	4.09	60	5.505	23	5.57	14	3.802	28	3.807	30	4.114	68	4.11	100
3.466	29	3.446	30	4.311	53	4.30	19	3.427	77	3.434	80	3.867	6	3.88	10
3.186	100	3.173	100	4.210	100	4.20	100	3.339	60	3.346	60	3.834	11	3.82	20
2.755	16	2.731	20	3.900	62	3.915	24	3.959	55	2.996	60	3.363	100	3.35	100
2.528	79	2.513	80	3.479	37	3.480	20	2.637	43	2.635	50	2.978	8	2.974	10
2.085	18	—	—	3.466	30	3.457	18	2.592	30	2.591	40	2.599	49	2.60	60
2.067	15	2.077	10	3.338	41	3.367	11	2.398	31	2.398	40	2.411	5	2.408	10
2.049	15	2.052	10	3.302	36	3.286	31	2.071	12	2.064	20	2.058	17	2.056	40
								2.058	22	2.054	30				
1.969	17	1.956	10	2.950	30	2.933	11	1.852	10	1.846	10	2.023	19	2.016	30
1.891	27	—	—	2.940	25	—	—	1.831	18	1.828	30	1.933	15	1.929	30
1.838	16	1.832	40	2.763	20	2.762	7					1.859	15	1.857	30

Pure, single phase samples of U_2MoO_8 were prepared by mixing calculated amounts of UO_2 with the $UMoO_6$ sample thus prepared and heating this mixture in an evacuated, sealed silica tube for 2–3 weeks at 973 K. The UMo_2O_8 sample was prepared by heating a mixture of UO_2/MoO_3 (1 : 2) at 873 K in a sealed, evacuated silica tube for 2–3 weeks.

As the formation of UMo_2O_8 is complete at 873 K, when there is no appreciable vaporization of MoO_3(s), this compound was first prepared and then used in the subsequent preparation of the $UMoO_5$ phase. A mixture of UMo_2O_8 and UO_2, in a specified ratio, was heated in an evacuated, sealed silica tube at 973 K for 2 weeks to obtain a single phase $UMoO_5$. Phase characterization of all solid samples was carried out by XRD using Cu K_α radiation. The *d* spacings of the samples agreed with those reported in the literature (Table 1).

The thermal stability of the compounds was studied using the microthermobalance system. Details of the apparatus and the procedure can be found

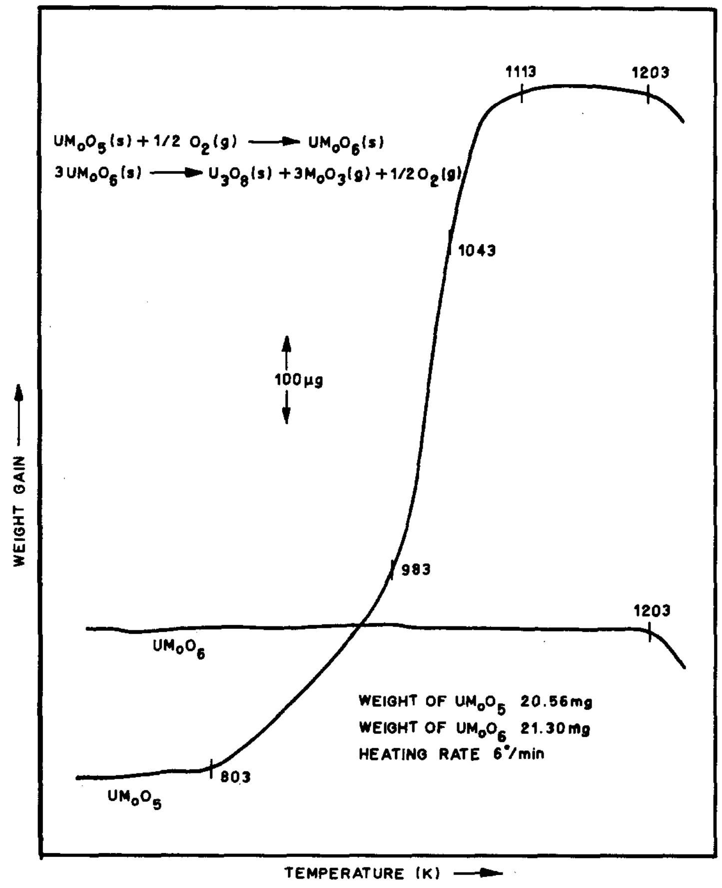

Fig. 1. Thermogravimetric curve for the oxidation of $UMoO_5$ to $UMoO_6$ in flowing dry air.

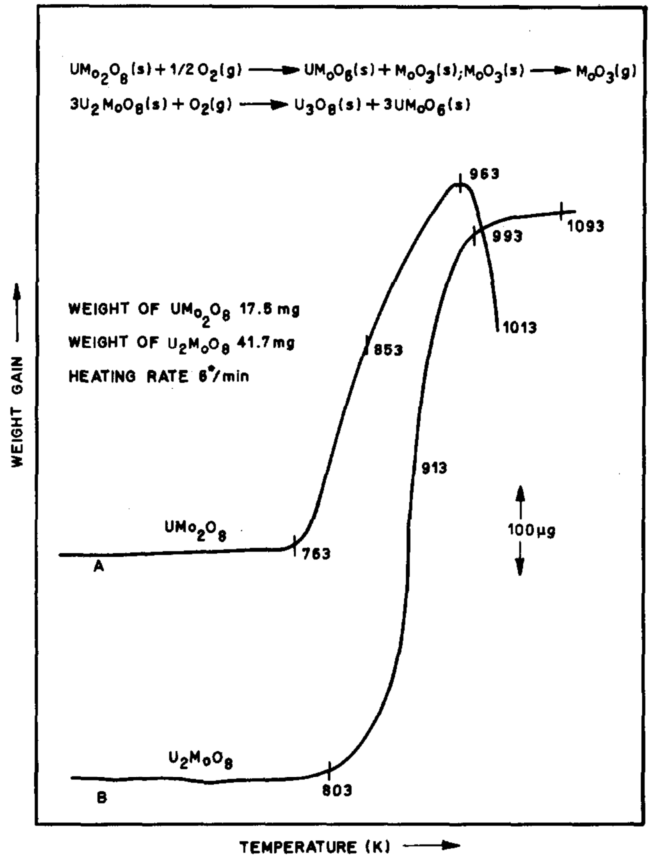

Fig. 2. Thermogravimetric curves for the oxidation of UMo_2O_8 and U_2MoO_8 in flowing dry air.

in the literature [10]. Samples (~ 20–40 mg) were placed in platinum cups and heated at 6 K min^{-1} in flowing gases (~ 2 l h^{-1}). Resultant TG curves are shown in Figs. 1 and 2.

RESULTS AND DISCUSSIONS

Figure 1 shows the TG curve of $UMoO_5(s)$ in flowing, dry air. The oxidation begins at ~ 800 ± 5 K and the rate appears to increase rapidly after 980 K. By ~ 1100 K, the oxidation is complete. The resultant product is thermally stable up to ~ 1200 K when there is a mass loss. The measured mass gain between 800 and 1100 K corresponds to the following reaction (Table 2)

$$UMoO_5(s) + \tfrac{1}{2}O_2(g) = UMoO_6(s) \qquad (1)$$

TABLE 2

Thermogravimetric data

Reactions	Percentage weight gain		Temperature range (K)
	Observed	Calculated	
(1) $UMoO_5(s) + \frac{1}{2} O_2(g)$ $\rightarrow UMoO_6(s)$	3.942	3.865	800–1100
(2) $U_2MoO_8(s) + \frac{1}{3} O_2(g)$ $UMoO_6(s) + \frac{1}{3} U_3O_8(s)$	1.631	1.524	800–1000
(3) $UMo_2O_8(s) + \frac{1}{2} O_2(g)$ $UMoO_6(s) + MoO_3(s)$	2.514 [a]	2.867	763–963

[a] The observed weight gain is less than the calculated one because the $MoO_{3(s)}$ formed starts to evaporate before the reaction is complete.

Above 1200 K, the $UMoO_6$ begins to decompose according to reaction (2)

$$UMoO_6(s) = \frac{1}{3} U_3O_8(s) + \frac{1}{6} O_2(g) + \frac{1}{3} (MoO_3)_3(g) \qquad (2)$$

Both $UMo_2O_8(s)$ and $U_2MoO_8(s)$ are oxidised to $UMoO_6(s)$ in air as shown in Fig. 2. However, in the case of UMo_2O_8, the oxidation to $UMoO_6$ is

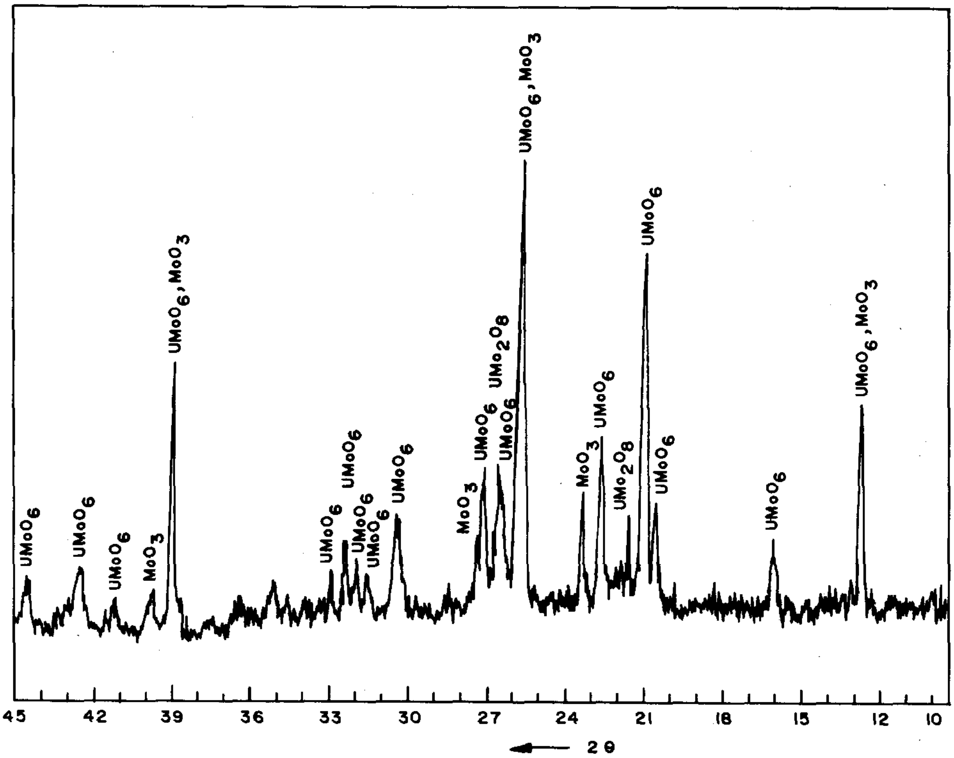

Fig. 3. X-ray diffraction pattern of the product obtained by heating UMo_2O_8 to 780 K in air for 1 h and subsequent quenching to room temperature.

accompanied by the formation of $MoO_3(s)$. Hence, above 960 K the TG curve shows a mass loss due to the vaporization of $MoO_3(s)$.

A sample of UMo_2O_8 heated in a separate experiment to 780 K in air for 1 h and then quenched, showed the presence of $UMoO_6(s)$ and $MoO_3(s)$ in addition to the unreacted $UMo_2O_8(s)$ phase on XRD examination (Fig. 3). Based on these observations, the following heterogeneous reactions are proposed for the thermal stabilities of the uranium molybdates in air

$$UMoO_5(s) + \tfrac{1}{2}\ O_2(g) \xrightarrow{(800 \pm 10\ K)} UMoO_6(s) \tag{1a}$$

$$UMoO_6(s) \xrightarrow{1200\ K} \tfrac{1}{3}\ U_3O_8(s) + \tfrac{1}{3}(MoO_3)_3(g) + \tfrac{1}{6}\ O_2(g) \tag{2a}$$

$$UMo_2O_8(s) + \tfrac{1}{2}\ O_2(g) \xrightarrow{760 \pm 10\ K} UMoO_6(s) + MoO_3(s) \tag{3}$$

$$MoO_3(s) \xrightarrow{960\ K} \tfrac{1}{3}\ (MoO_3)_3(g) \tag{4}$$

$$U_2MoO_8(s) + \tfrac{1}{3}\ O_2(g) \xrightarrow{800 \pm 10\ K} UMoO_6(s) + \tfrac{1}{3}U_3O_8(s) \tag{5}$$

These results clearly show that in air only the $UMoO_6(s)$ phase is stable up to 1200 K and all others are oxidised to this phase.

ACKNOWLEDGEMENTS

The authors thank Dr. K.N. Rao, Head, Chemical Group and Dr. K.S. Venkateswarlu, Head, Water Chemistry Section for their interest and encouragement in this work.

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