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THERMAL STABILITY OF U_3O_8 IN AIR AT HIGH TEMPERATURE

S. R. Dharwadkar, M. S. Chandrasekharaiah and M.D. Karkhanavala

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 India

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In spite of several reports in literature [1–4] about the nonstoichiometry of U_3O_8-phase above 770 K, the simple ignition at 1125 K in air as a method of O/U analysis of urania is continued to be employed [5–9] on the assumption the resultant product is stoichiometric U_3O_8. Lynch's [1] observation that this phase exhibits significant oxygen deficiency in air above 770 K was substantiated in this laboratory [10] earlier by a simple batch process up to 1125 K. In the present communication we report the results of a microthermogravimetric study of the thermal stability of U_3O_8 phase in air up to 1275 K employing a microthermobalance designed and constructed [11] in our laboratory.

Experimental

A microthermobalance operable at 1 μg sensitivity in static air and at 5 μg in flowing air (3.5 l/hr) was used. The hygroscopic nature of $< U_3O_8 >$ necessitated the preparation of this phase of known composition in situ. Previously in this laboratory it was established that the composition of $< U_3O_8 >$ phase formed in air

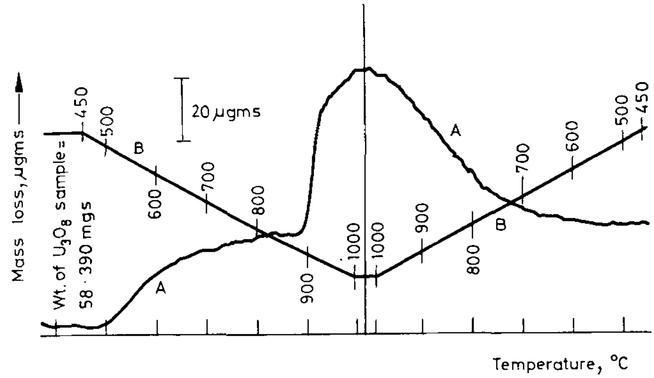

Fig. 1. A typical thermogravimetric curve (1 μgm sensitivity) for U_3O_8 in air. A — mass loss trace, B — temperature trace

by the oxidation of urania sample [10, 12] and by the decomposition of β-UO_3 [13] or by the careful oxidation of uranium metal was invarient of the pre-history of the starting sample but was determined by the temperature alone. Hence the exact composition of the U_3O_8-phase formed at 725 K in air by the oxidation of nuclear pure urania ($UO_{2.02}-UO_{2.04}$, total metallic impurities less than 200 ppm) samples was established as $UO_{2.671+.002}$ in a separate experiment. The U_3O_8-phase was identified as the orthorhombic form by X-ray powder diffraction method.

In each TG run, 50–60 mg of this nuclear pure urania sample was taken in a platinum bucket and oxidized in situ at 725 K in air for nearly 24 hours. Then the resulting product was thermal cycled between 725 and 1275 K. A typical TG curve obtained in air is shown in Fig. 1. The TG curve in flowing gas remains essentially the same except for the reduction in sensitivity.

Results and discussion

It is seen from Fig. 1 that the O/U ratio of the U_3O_8 phase decreased somewhat sharply between 770–1025 K and then gradually between 1025–1125 K. But above 1165 K there is a second very rapid loss up to 1275 K. From the observed mass change, and the a priori knowledge of the composition at 725 K, the O/U compositions of this phase as a function of temperature was calculated and is shown in Fig. 2. The present observation confirms our earlier report [10] regarding the oxygen deficiency of the high temperature U_3O_8-phase up to 1125 K. But the observed second rapid mass loss around 1165 K could not be predicted either from our earlier data, or from the extrapolated thermodynamic data given by

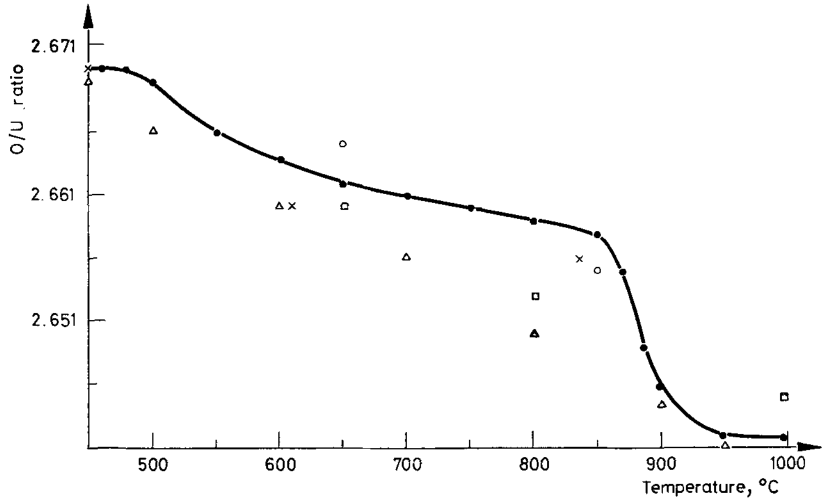

Fig. 2. Composition of U_3O_8 in air as a function of temperature. — • — present work, — △ — Lynch data — □ — Gobo's data, — × — volumetric data (this Lab.) from UO_{2+x} ignition, — ○ — volumetric data (this Lab) from UO_3 decomposition

Rand and Kubaschewski [13]. This differs also from the report of Lynch [1] who reported a continuous rather than the stepwise process. This mass loss is not due to any significant loss of uranium bearing vapour species since on cooling even at a rate of 10°/min almost the entire mass loss that occurred during this second step is regained. Further support for this contention was obtained when the TG was taken in 1 atmosphere of pure oxygen. There was an increase of twenty degrees in the temperature of inception of the first step but there was nearly a hundred degree enhancement in the initiation temperature of the second step. Yet, the relative mass loss of the second step remained the same. Both these observations rule out any significant contribution to the observed mass loss by uranium containing vapour species. When the sample was maintained at 1275 K there was no further loss in mass as seen in Fig. 1, supporting the fact that the observed mass loss is due to oxygen.

The exact nature of this transformation is still not clear. However, an endothermic peak around 1173 K was observed in a DTA study in air. Similar DTA peak was reported earlier by Lynch [14]. Malinin and Tolmachev [15] have reported a DTG peak around 1143 K which they attributed to the conversion of U_3O_{8-x} to U_8O_{21}. Work is in progress to elucidate the nature of this transformation. Even though the entire oxygen loss of the sample between 1165 and 1275 K was recovered on cooling to 1100 K or below, the oxygen loss between 725 and 1100 K was not recovered even after several hours of reheating at 725 K. This confirms our earlier conclusion [10] that the usual analytic method of heating in air at 1123 K for the O/U analysis on the assumption of stoichiometric U_3O_8 does not yield reliable data.

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