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# A STUDY OF THE NON-STOICHIOMETRY IN $U_3O_8$

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## ABSTRACT

Measurements of the oxygen-to-uranium ratio in $U_3O_8$ were performed using two independent methods, namely thermogravimetry and wet chemical analysis by cerimetry. The O/U variations in $U_3O_8$ were delineated as a function of temperature in the range 450–900 °C. The experimental conditions for the attainment of the stoichiometric state were also examined.

## INTRODUCTION

A study of the compositional variations in $U_3O_8$ is interesting from the point of view of the delineation of the phase boundary of this non-stoichiometric compound and the establishment of a reference state for O/U measurements on uranium oxides. Since $U_3O_8$ is a starting material in the production of nuclear fuels, its exact composition also has technological implications.

$U_3O_8$ is known to be non-stoichiometric and the departure from stoichiometry is a function of temperature and ambient oxygen pressure. Dharwadkar et al. [1], Fujino et al. [2] and Ackermann and Chang [3] have investigated the temperature–composition relationships of this oxide, but disagreement still exists on the variation in the oxygen-to-uranium ratio of the equilibrium phase produced in air as a function of temperature. The conditions which lead to the stoichiometric state are also not clearly defined. Payne [4], Javed [5] and Petit and Kienberger [6] obtained stoichiometric $U_3O_8$ at 800–850 °C, whereas Lynch et al. [7] and other investigators [8,9] obtained the same at 600 °C.

In this study, measurement of the variation in the stoichiometry of $U_3O_8$ in air was carried out as a function of temperature in the range 450–900 °C using two independent techniques for O/U determination, namely thermo-

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gravimetry and chemical analysis by cerimetry. The O/U ratio of $U_3O_8$ was measured in air by thermogravimetry in situ as a function of temperature. In a separate set of experiments the O/U ratio of $U_3O_8$, formed by oxidation of $UO_2$ followed by cooling in air or argon, was determined using cerimetry.

## EXPERIMENTAL

### *Thermogravimetric studies*

The thermogravimetric measurements were carried out using a Netzsch model STA 429 thermal analyser. For each of the thermogravimetric runs, $U_3O_8$ was obtained by heating nuclear grade uranium dioxide (supplied by Atomic Fuels Division, BARC, Bombay) at 450 °C in air for 6 h, followed by cooling to room temperature and loading into the thermal analyser. The weight changes experienced by the sample on heating in air from room temperature to a set temperature were recorded. Each time a fresh sample was taken, and the weight change was measured up to the set temperature. In this manner the in situ O/U ratios at various temperatures in the range 450–900 °C were obtained. The O/U ratio of the starting material at room temperature was determined using the $H_2/H_2O$ gas equilibration technique [10]; the samples in this case were handled in the same manner as those used for oxidation in air.

### *Cerimetric measurements*

The cerimetric method used for the determination of the O/U ratio of $U_3O_8$ was a modification of the method reported earlier by Dharwadkar and Chandrasekharaiah [11]. The $U_3O_8$ sample was weighed and was then dissolved in a known excess of a solution of cerium(IV) sulphate in sulphuric acid at 70 °C. Cerium(IV) in the solution oxidized $U^{IV}$ to $U^{VI}$. In order to determine the $Ce^{IV}$ left in the solution, a known excess of $Fe^{II}$ sulphate solution was added and the excess $Fe^{II}$ was titrated against standard potassium dichromate solution. The end point was determined potentiometrically, and with a knowledge of the $U^{IV}$ content of the sample, the O/U ratio was calculated. In this work, samples of $UO_2$ were taken and heated at a selected temperature in air in a laboratory furnace for 6 h. The $U_3O_8$ formed was cooled in air and its O/U ratio was determined by the cerimetric procedure described above. Measurements were performed at various selected temperatures in the range 450–900 °C. In a few cases cooling of the samples was carried out in argon in order to examine the O/U ratios obtained under conditions of no oxygen absorption.

## RESULTS AND DISCUSSION

Results of the O/U measurements on $U_3O_8$ from thermogravimetry and cerimetric analysis are given in Table 1. The variation in the O/U ratio of $U_3O_8$ as a function of temperature is shown in Fig. 1 together with literature data. It can be seen that the O/U values from thermogravimetry and the cerimetry results obtained on the argon-cooled samples agree well with each other. These data together represent the in situ O/U ratios and are indicated as curve B in Fig. 1. The O/U values obtained for the air-cooled $U_3O_8$ samples are indicated as curve A in the same figure. It can be seen that the O/U values represented by curve A are higher than the in situ values represented by curve B, thus indicating that oxygen absorption during cooling is an important factor. It can be seen in Fig. 1 that the in situ O/U data from this work are generally higher than the results of Dharwadkar et al. [1] below 750 °C and of Ackermann and Chang [3] throughout the temperature range. A detailed discussion on the variation in O/U ratio as a function of temperature and the phase behaviour of $U_3O_8$ has been presented by Dharwadkar et al. [12]. The cerimetric method for O/U measurement used here is considered to be a refinement of that used by earlier investigators [11]. In the procedure used here errors that can arise due to the oxidation of water by $Ce^{4+}$ were eliminated by carrying a blank through the procedure, potassium dichromate was used as titrant instead of ferrous ammonium sulphate and a potentiometric method of end-point determination was employed instead of the visual indicator.

It can also be seen from Fig. 1 that the in situ O/U ratio of $U_3O_8$ (curve B) in air decreases from a hyperstoichiometric value of 2.684 at 450 °C to the stoichiometric value of 2.667 at 650 °C. As the temperature is further increased the O/U ratio decreases progressively to hypostoichiometric values. However, as seen from curve A, the O/U values of air-cooled $U_3O_8$ are higher. The stoichiometric state is reached at 750–800 °C and a subsequent

TABLE 1

Data from O/U measurements on $U_3O_8$ at various temperatures

| Measurement technique | O/U ratio | | | | | |
|---|---|---|---|---|---|---|
| | 450 °C | 500 °C | 600 °C | 700 °C | 800 °C | 900 °C |
| From thermogravimetry | 2.684 | 2.683 | 2.676 | 2.664 | 2.661 | 2.651 |
| From cerimetry (air-cooled samples) | 2.699 [a] | 2.696 | 2.677 [b] | 2.668 | 2.665 | 2.664 |
| From cerimetry (argon-cooled samples) | 2.683 | – | 2.675 [b] | – | 2.658 [c] | – |

[a] 470 °C. [b] 610 °C. [c] 850 °C.

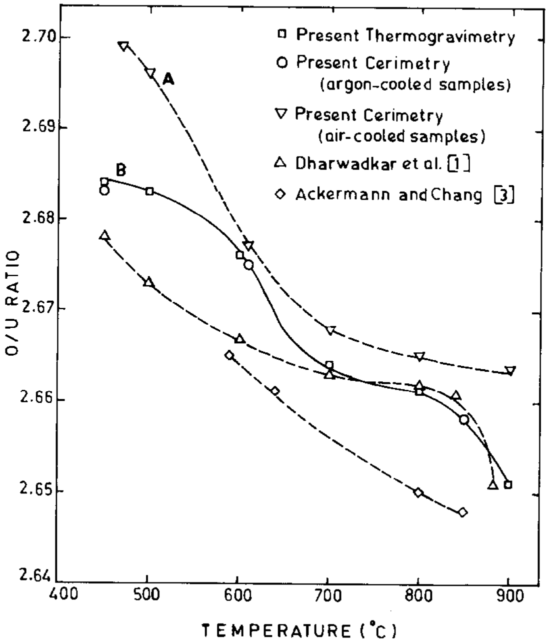

Fig. 1. Oxygen-to-uranium ratio in $U_3O_8$ as a function of temperature.

increase in temperature results in only a very slow decrease in O/U ratio. These are important observations as they help to rationalize the discrepancy mentioned earlier regarding the conditions for the attainment of the stoichiometric state. From this study, it can be seen that the stoichiometric O/U ratio can be achieved at 650 °C under conditions of in situ measurement, whereas a temperature of 750–800 °C can be employed under the common laboratory conditions of heating and cooling in air. The exhibition of hyperstoichiometry by $U_3O_8$ at temperatures less than 650 °C merits further attention. While the average uranium valency at 600 °C is 5.35 from this work, in an earlier study from our laboratory [13] it was found that in $U_3O_8$ containing small amounts of dissolved cerium, the average uranium valency stabilized at a value of 5.5 at 600 °C. Thus it appears that under favourable conditions, the hyperstoichiometry in $U_3O_8$ can be significantly high.

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