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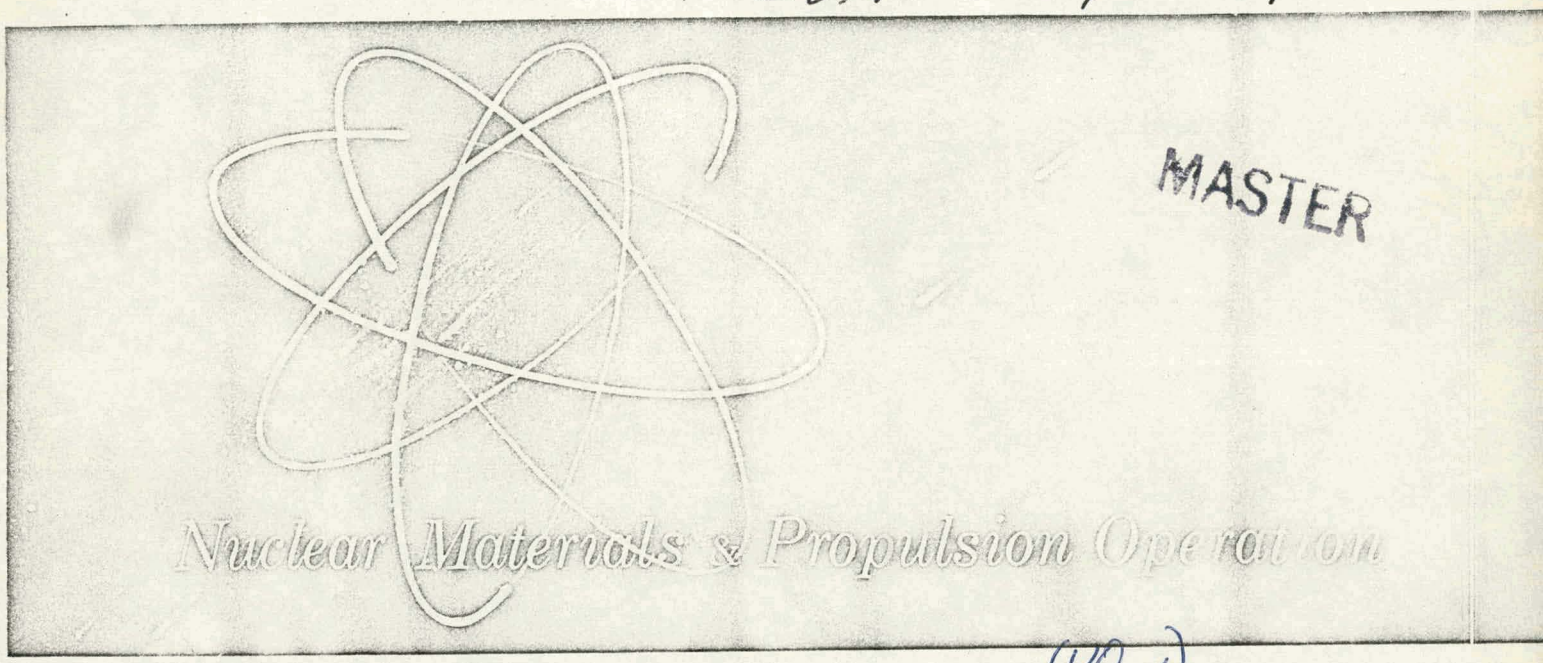

CHARACTERISTICS OF SUBSTOICHIOMETRIC URANIA (UO_{2-x}) AT ELEVATED TEMPERATURES

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CHARACTERISTICS OF SUBSTOICHIOMETRIC URANIA (UO_{2-x}) AT ELEVATED TEMPERATURES

by E. A. Aitken, H. C. Brassfield, J. A. McGurty

Recent reports have indicated that after heating UO_2 in inert or reducing atmospheres to temperatures above 1700°C, uranium metal is present as a finely dispersed phase in UO_2. Rothwell has proposed that the uranium appears as a result of precipitation of the metal from a substoichiometric UO_{2-x} phase. On cooling, the degree of substoichiometry changes gradually towards the stoichiometric value. Rothwell's measurements were below 2000°C where the degree of substoichiometry was not large. In the work at GE-NMPO, we have observed precipitation of free uranium metal in greater quantities after sintering of UO_2 pellets at temperatures in excess of 2000°C.

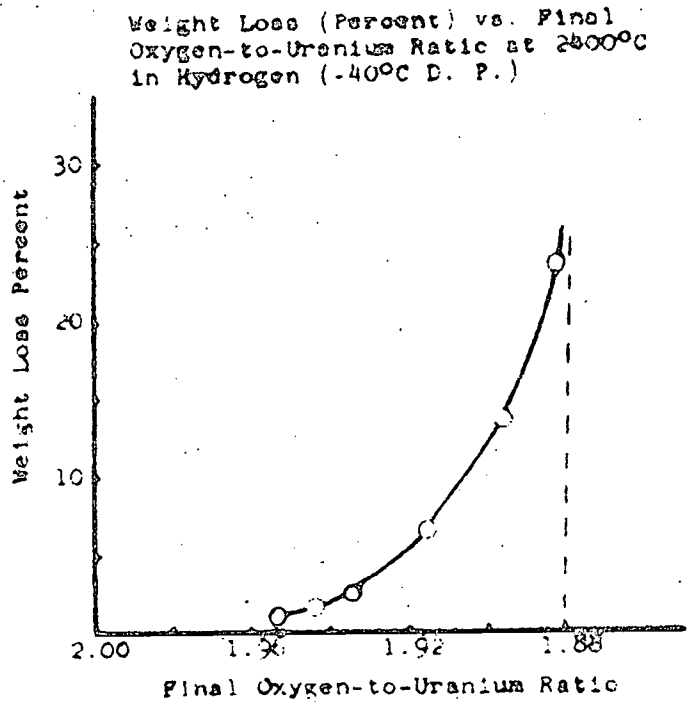
Metallographic examination of UO_2, heated to 2000°C and above in reducing or inert atmospheres and then cooled to room temperature, showed the material to be two phase, UO_2 and uranium. It was suspected that the UO_2 fluorite lattice became oxygen deficient at elevated temperature and exhibited a chemical behavior analogous to other oxide compounds with the fluorite structure. In order to more fully understand the chemistry of UO_2 at these temperatures, a series of experiments was performed aimed at correlating the volatility of UO_2 with the degree of oxygen deficiency over a range of temperatures and times. Pellets of UO_2 were heated at temperatures of 2200°C to 2600°C in an open rhenium crucible in a flowing hydrogen atmosphere. Helium was used as a purging gas on cooling below 1500°C, to prevent hydriding of any free uranium which may have precipitated.

The weight loss and the final oxygen-to-uranium ratio were determined after each run and a portion of the specimen was examined metallographically. The results, summarized in Table I, show that at higher temperatures greater weight losses and lower oxygen-to-uranium ratios were obtained. The same trend was observed for longer times at temperature.

A second series of experiments was run in which a pre-sintered UO_2 pellet was suspended by a rhenium wire in the hot zone of a hydrogen furnace at 2400°C for a given period of time. These experiments, as expected, showed higher loss rates than pellets heated in the open crucible.

Congruent Vaporization - Figure 1 is a plot of the percent weight loss of the pellet against the final oxygen-to-uranium ratio at 2400°C in hydrogen (-40°C D.P.). The final composition appears to be approaching a congruent vapor composition of $UO_{1.88}$. A pellet which contained both a mixture of uranium and UO_2 was prepared at an oxygen-to-uranium ratio of 1.75. When this pellet was heated in an open crucible at 2600°C in dry hydrogen to volatilize a considerable fraction of the pellet, the final oxygen-to-uranium ratio was found to be 1.89 which is in agreement with a similar experiment starting with UO_2. Therefore, the congruent vaporization composition of $UO_{1.89}$ is an equilibrium value. When the pellets were suspended in an atmosphere of helium, the loss rates were comparable to hydrogen, but the final oxygen-to-uranium ratio was only 1.94. From phase rule considerations, the congruent vaporization point is a function of both temperature and oxygen partial pressure. Thus, a higher partial pressure of oxygen in helium than in a dry hydrogen atmosphere would shift the congruent vapor composition towards the

Figure 1


Weight Loss (Percent) vs. Final Oxygen-to-Uranium Ratio at 2600°C in Hydrogen (-40°C D. P.)
Weight Loss Percent
30
20
10
2.00
1.96
1.92
1.88
Final Oxygen-to-Uranium Ratio

stoichiometric (UO_2) value.

There are two possible chemical equations which the substoichiometric phase can be produced as shown in Figure 2.

1. If the UO_2 is virtually reduced by the hydrogen, only oxygen will be removed from the pellet. The percent weight loss per unit change in x will be a constant independent of x. The constant would be equal to 5.92.

2. If the uranium gases are the major source of preferential removal of oxygen, then equation 2 of Figure 2 will control the loss fraction versus oxygen deficiency curve. This function will be variable with x. The UO_y gas composition is a composite mixture of UO_3, UO_2, UO and to a lesser extent O_2.

The data in Table 1 may be used to generate $(\frac{\Delta W}{\Delta X})^{-1}$ and x' for the measurements at 2400°C in hydrogen. The values for $(\frac{\Delta W}{\Delta X})^{-1}$ range from a maximum value of 0.42 to 0.0014 near the congruent point as shown in Figure 3. These data indicate that equation 2 is probably the mechanism in which a high degree of substoichiometry is produced. Near the $UO_{2.00}$ side the data are strongly influenced by errors in measurement and it is difficult to make a choice between which of the two possible equations is causing the formation of UO_{2-x} phase.

Evidence for Non-Existence of Free Uranium Metal at 2400°C - It has been proposed that free uranium metal precipitates from a UO_{2-x} phase on cooling because of a decrease in x with decreasing temperatures. The supposition that there is no free uranium metal at temperatures of 2400°C for compositions around $UO_{1.88}$ has not been

FIGURE 2

1. $UO_{2-x} \longrightarrow \frac{x' - x}{2} O_2 + UO_{2-x'}$

$\frac{\Delta W}{\Delta X} = 5.92$ $\qquad$ $(\frac{\Delta W}{\Delta X})^{-1} = 0.169$

2. $UO_{2-x} \longrightarrow \Delta W\ UO_{y(s)} + (1 - \Delta W)\ UO_{2-x'}$

$\frac{\Delta W}{\Delta X} = \frac{1}{y - (2 - x')}$ $\qquad$ $(\frac{\Delta W}{\Delta X})^{-1} = y - (2 - x')$

TABLE I

SUMMARY (OF THE VOLATILITY EXPERIMENTS) OF UO_2 PELLETS

Experiment	Container	Atm.	Temp. (°C)	Time (hr.)	Percent[a] Loss in Wt.	Final[b] O/U Ratio
1	Re	H_2	2200	4	0.7	1.96$_0$
2	Re	H_2	2400	1	1.1	1.95$_4$
3	Re	H_2	2400	2	1.6	1.94$_8$
4	Re	H_2	2400	4	2.6	1.93$_5$
5	Re	H_2	2600	4	20	1.89$_9$
6	none	H_2	2400	2/3	6.6	1.91$_6$
7	none	H_2	2400	2	13.5	1.89$_6$
8	none	H_2	2400	4	23.3	1.88$_2$
9	none	He	2400	2/3	Lost	2.00$_7$
10	none	He	2400	4	24.4	1.94$_2$

a. For experiments run in the rhenium crucible, the measured loss was decreased by 0.5% due to the reduction of $UO_{2.09}$ to $UO_{2.00}$ during the heat-up cycle. No correction was necessary for the experiments where the pellet was suspended.

b. The oxygen-to-uranium ratio was determined by measuring the weight change on oxidation of a 15 gm pellet in air to constant weight at 900°C. Assuming that the oxidized product is $UO_{2.67}$, the initial O/U ratio was determined from the weight change. The method is considered accurate to 0.005 units in O/U ratio.

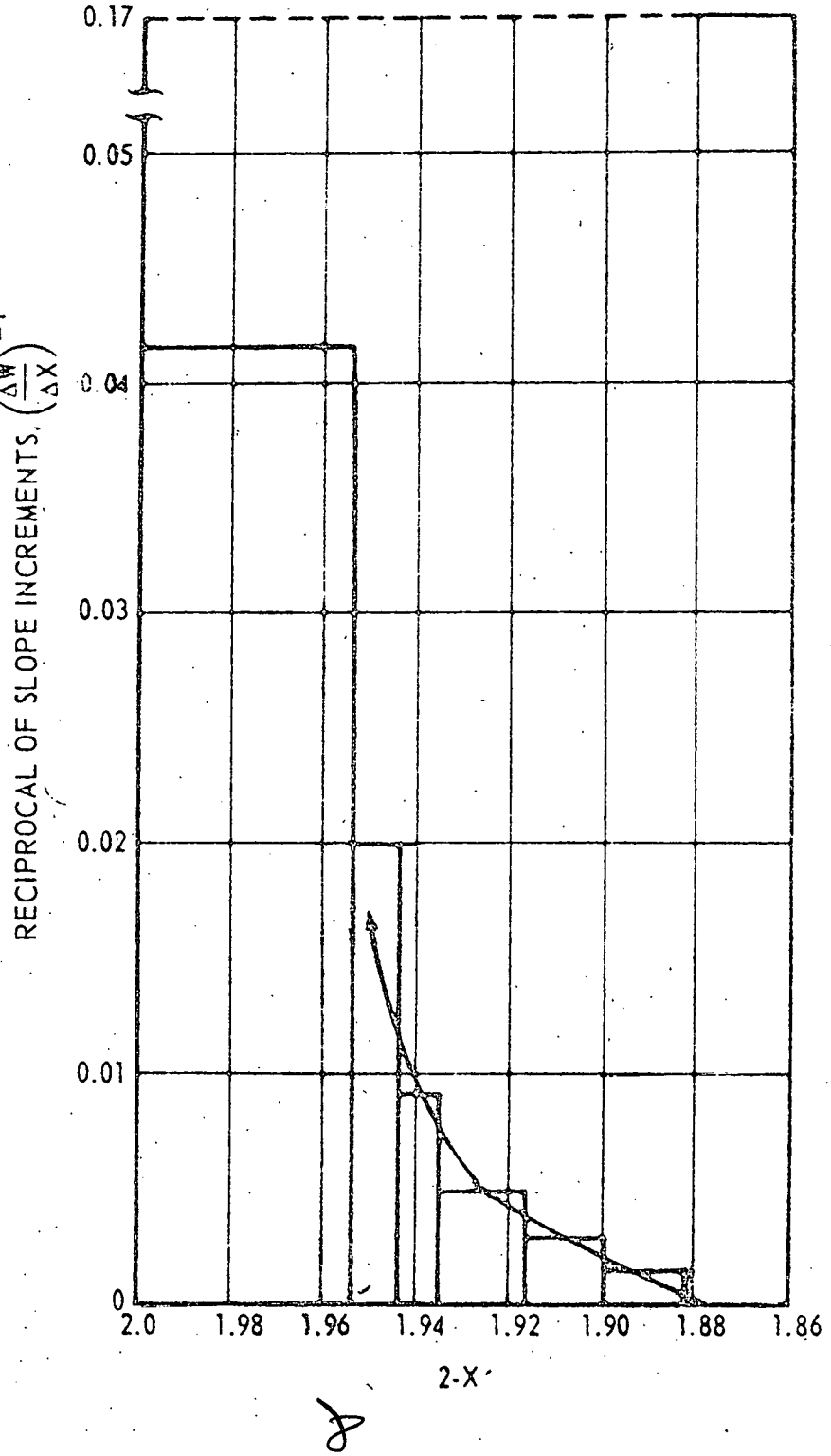

0.17
0.05
0.04
0.03
0.02
0.01
0
RECIPROCAL OF SLOPE INCREMENTS, $\left(\frac{\Delta W}{\Delta X}\right)^{-1}$
2.0
1.98
1.96
1.94
1.92
1.90
1.88
1.86
2-X'

FIGURE 3

confirmed by direct observation. Indirect evidence, however, has been obtained that there is no uranium metal present in UO_{2-x} ($x < 0.11$) since rhenium wire in contact with these pellets showed no tendency to melt and break. Separate experiments where the uranium was known to be present in the UO_2 pellet above 2200°C showed very rapid melting and attack of the rhenium wire.

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