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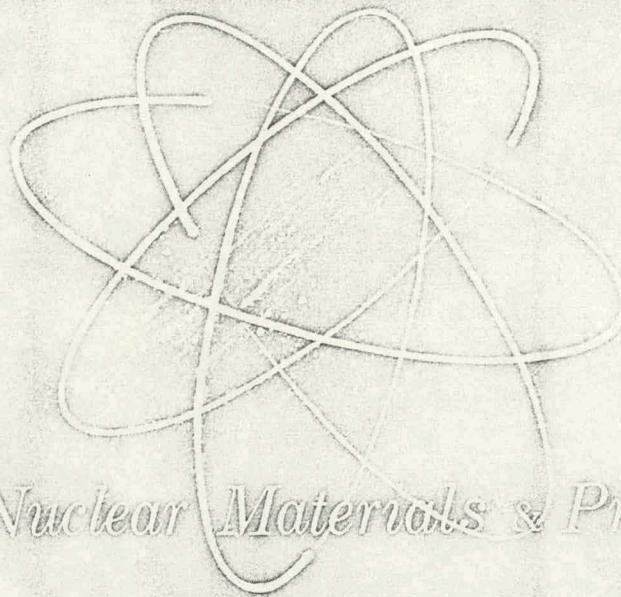
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(UO₂-x)

CHARACTERISTICS OF SUBSTOICHIOMETRIC URANIA 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 $1700^\circ C$, 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 $2000^\circ C$ 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 $2000^\circ C$.

Metallographic examination of UO_2 , heated to $2000^\circ C$ 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 $2200^\circ C$ to $2600^\circ C$ in an open rhenium crucible in a flowing hydrogen atmosphere. Helium was used as a purging gas on cooling below $1500^\circ C$, to prevent hydriding of any free uranium which may have precipitated.

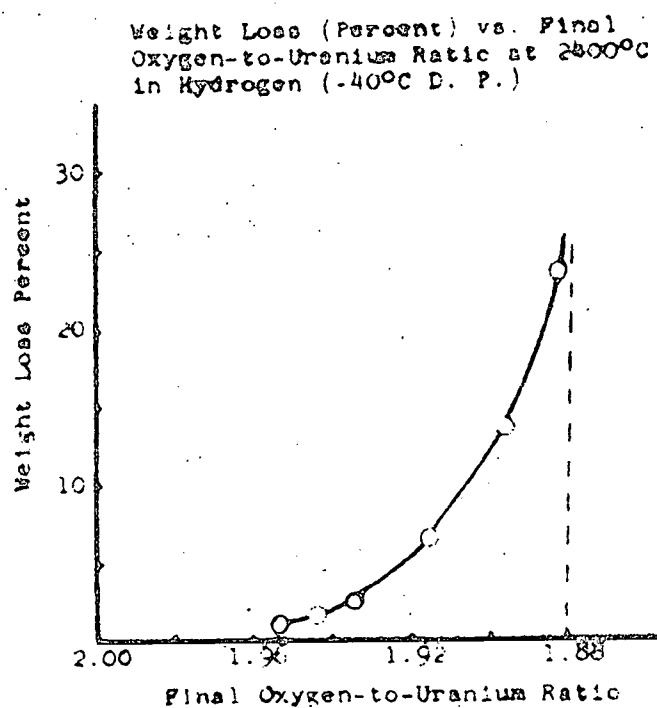
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The weight loss and the final oxygen-to-uranium ratio were determined after each run and a portion of the specimen was examined metallographically. The results, summarized in Table I, show that at higher temperatures greater weight losses and lower 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 $2400^{\circ}C$ 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 $2400^{\circ}C$ in hydrogen ($-40^{\circ}C$ 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 $2600^{\circ}C$ 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



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stoichiometric (UO_2) value.

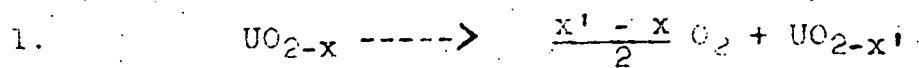
There are two possible chemical equations which the substoichiometric phase can be produced as shown in Figure 2.

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 .

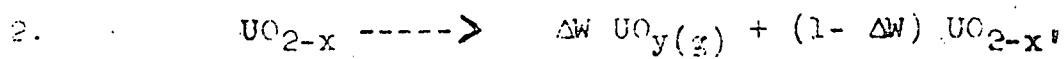
The data in Table 1 may be used to generate $(\frac{\Delta W}{\Delta X})^{-1}$ and x' for the measurements at 2400°C in hydrogen. The values for $(\frac{\Delta W}{\Delta X})^{-1}$ range from a maximum value of 0.42 to 0.0014 near the congruent point as shown in Figure 3. These data indicate that equation 2 is probably the mechanism in which a high degree of substoichiometry is produced. Near the UO_2 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



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



$$\frac{\Delta W}{\Delta X} = \frac{1}{y - (2 - x^1)} \quad \left(\frac{\Delta W}{\Delta X}\right)^{-1} = y - (2 - x^1)$$

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	1.960
2	Re	H_2	2400	1	1.1	1.954
3	Re	H_2	2400	2	1.6	1.934
4	Re	H_2	2400	4	2.6	1.935
5	Re	H_2	2600	4	20	1.699
6	none	H_2	2400	2/3	6.6	1.916
7	none	H_2	2400	2	13.5	1.896
8	none	H_2	2400	4	23.3	1.882
9	none	He	2400	2/3	Lost	2.007
10	none	He	2400	4	24.4	1.942

a. For experiments run in the muenium crucible, the measured loss was decreased by 0.5% due to the reduction of UO_2 .09 to UO_2 .90 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.

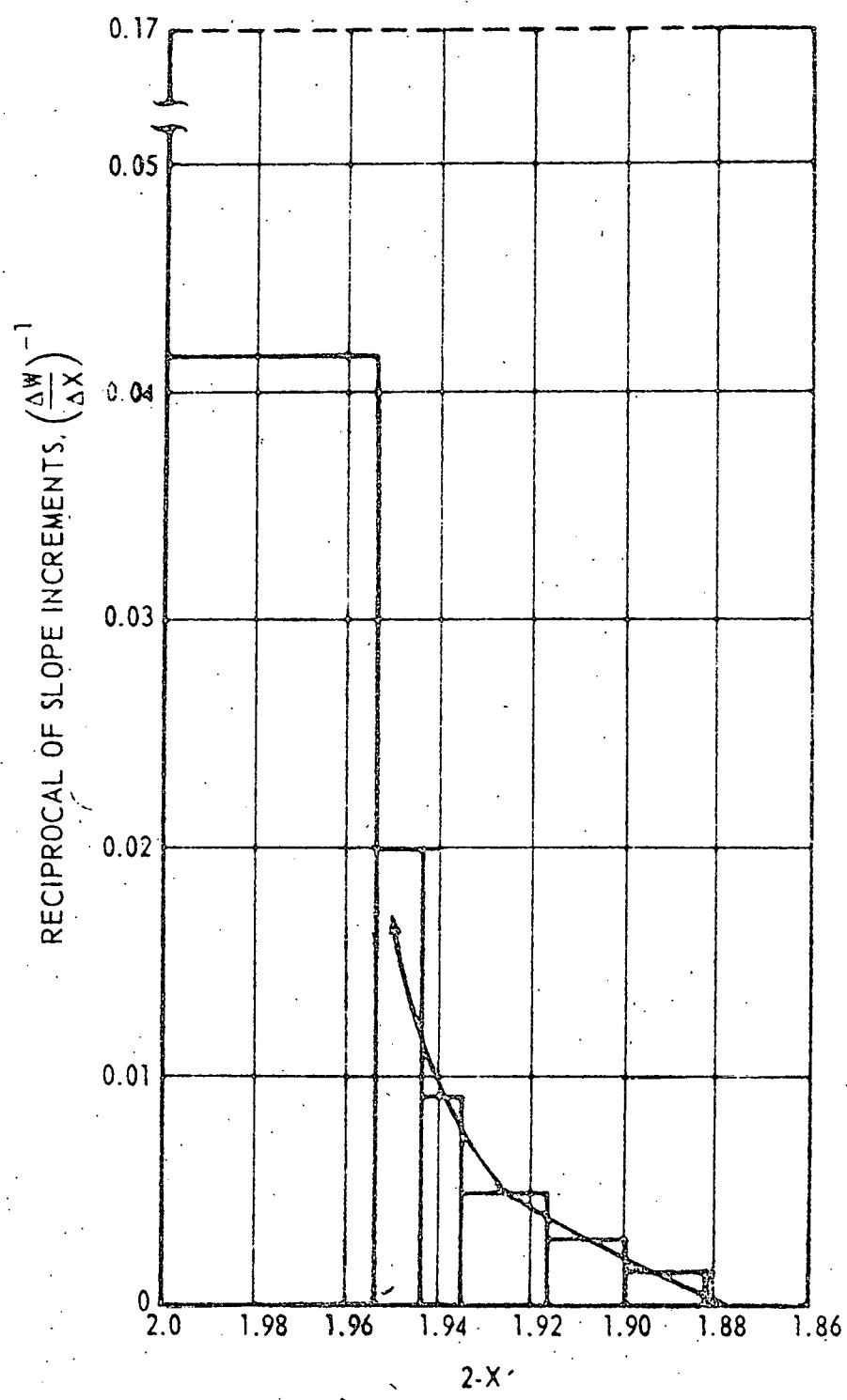


FIGURE 3

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 $2200^{\circ}C$ showed very rapid melting and attack of the rhenium wire.

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