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CHARACTERISTICS OF SUBSTOICHIOMETRIC URANIA <sup>(UO<sub>2-x</sub>)</sup> AT ELEVATED  
TEMPERATURES 1

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- 2 -

CHARACTERISTICS OF SUBSTOICHIOMETRIC URANIA ( $\text{UO}_{2-x}$ )  
AT ELEVATED TEMPERATURES

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

Recent reports have indicated that after heating  $\text{UO}_2$  in inert or reducing atmospheres to temperatures above  $1700^\circ\text{C}$ , uranium metal is present as a finely dispersed phase in  $\text{UO}_2$ . Rothwell has proposed that the uranium appears as a result of precipitation of the metal from a substoichiometric  $\text{UO}_{2-x}$  phase. On cooling, the degree of substoichiometry changes gradually towards the stoichiometric value. Rothwell's measurements were below  $2000^\circ\text{C}$  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  $\text{UO}_2$  pellets at temperatures in excess of  $2000^\circ\text{C}$ .

Metallographic examination of  $\text{UO}_2$ , heated to  $2000^\circ\text{C}$  and above in reducing or inert atmospheres and then cooled to room temperature, showed the material to be two phase,  $\text{UO}_2$  and uranium. It was suspected that the  $\text{UO}_2$  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  $\text{UO}_2$  at these temperatures, a series of experiments was performed aimed at correlating the volatility of  $\text{UO}_2$  with the degree of oxygen deficiency over a range of temperatures and times. Pellets of  $\text{UO}_2$  were heated at temperatures of  $2200^\circ\text{C}$  to  $2600^\circ\text{C}$  in an open rhenium crucible in a flowing hydrogen atmosphere. Helium was used as a purging gas on cooling below  $1500^\circ\text{C}$ , to prevent hydriding of any free uranium which may have precipitated.

2

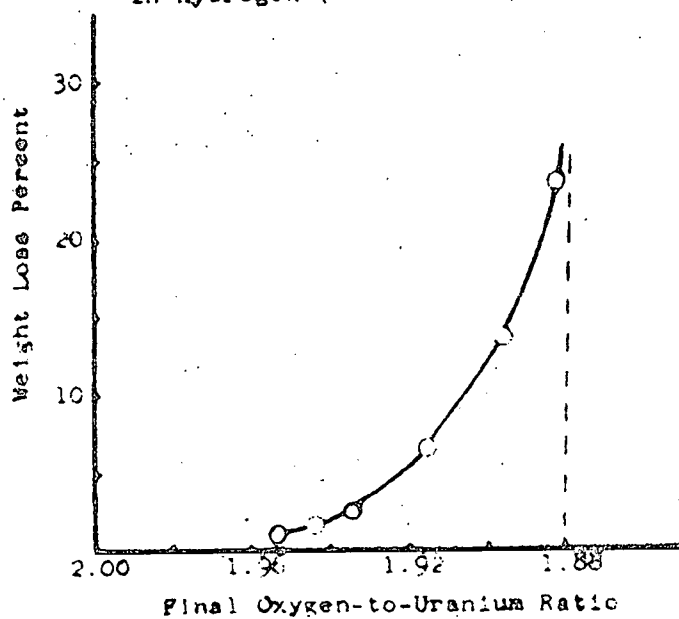
The weight loss and the final oxygen-to-uranium ratio were determined after each run and a portion of the specimen was examined metallographically. The results, summarized in Table 1, show that at higher temperatures greater weight losses and lower oxygen-to-uranium ratios were obtained. The same trend was observed for longer times at temperature.

A second series of experiments was run in which a pre-sintered  $\text{UO}_2$  pellet was suspended by a rhenium wire in the hot zone of a hydrogen furnace at  $2400^\circ\text{C}$  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  $2400^\circ\text{C}$  in hydrogen ( $-40^\circ\text{C}$  D.P.). The final composition appears to be approaching a congruent vapor composition of  $\text{UO}_{1.88}$ . A pellet which contained both a mixture of uranium and  $\text{UO}_2$  was prepared at an oxygen-to-uranium ratio of 1.75. When this pellet was heated in an open crucible at  $2600^\circ\text{C}$  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  $\text{UO}_2$ . Therefore, the congruent vaporization composition of  $\text{UO}_{1.89}$  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 2400°C  
in Hydrogen (-40°C D. P.)



stoichiometric ( $\text{UO}_2$ ) value.

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

1. If the  $\text{UO}_2$  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  $\text{UO}_y$  gas composition is a composite mixture of  $\text{UO}_3$ ,  $\text{UO}_2$ ,  $\text{UO}$  and to a lesser extent  $\text{O}_2$ .

The data in Table 1 may be used to generate  $(\frac{\Delta W}{\Delta X})^{-1}$  and  $x'$  for the measurements at  $2400^\circ\text{C}$  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  $\text{UO}_{2.00}$  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  $\text{UO}_{2-x}$  phase.

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

FIGURE 2

$$1. \quad \text{UO}_{2-x} \text{ -----} \rightarrow \frac{x' - x}{2} \text{O}_2 + \text{UO}_{2-x'}$$

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

$$2. \quad \text{UO}_{2-x} \text{ -----} \rightarrow \Delta W \text{UO}_y(\text{g}) + (1 - \Delta W) \text{UO}_{2-x'}$$

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



TABLE 1

SUMMARY (OF THE VOLATILITY EXPERIMENTS) OF  $UO_2$  PELLETS

Experiment	Container	Atm.	Temp. (°C)	Time (hr.)	Percent <sup>a</sup> Loss in Wt.	Final <sup>b</sup> O/U Ratio
1	Re	H <sub>2</sub>	2200	4	0.7	1.960
2	Re	H <sub>2</sub>	2400	1	1.1	1.954
3	Re	H <sub>2</sub>	2400	2	1.6	1.944
4	Re	H <sub>2</sub>	2400	4	2.6	1.935
5	Re	H <sub>2</sub>	2600	4	20	1.839
6	none	H <sub>2</sub>	2400	2/3	6.6	1.916
7	none	H <sub>2</sub>	2400	2	13.5	1.896
8	none	H <sub>2</sub>	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 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.

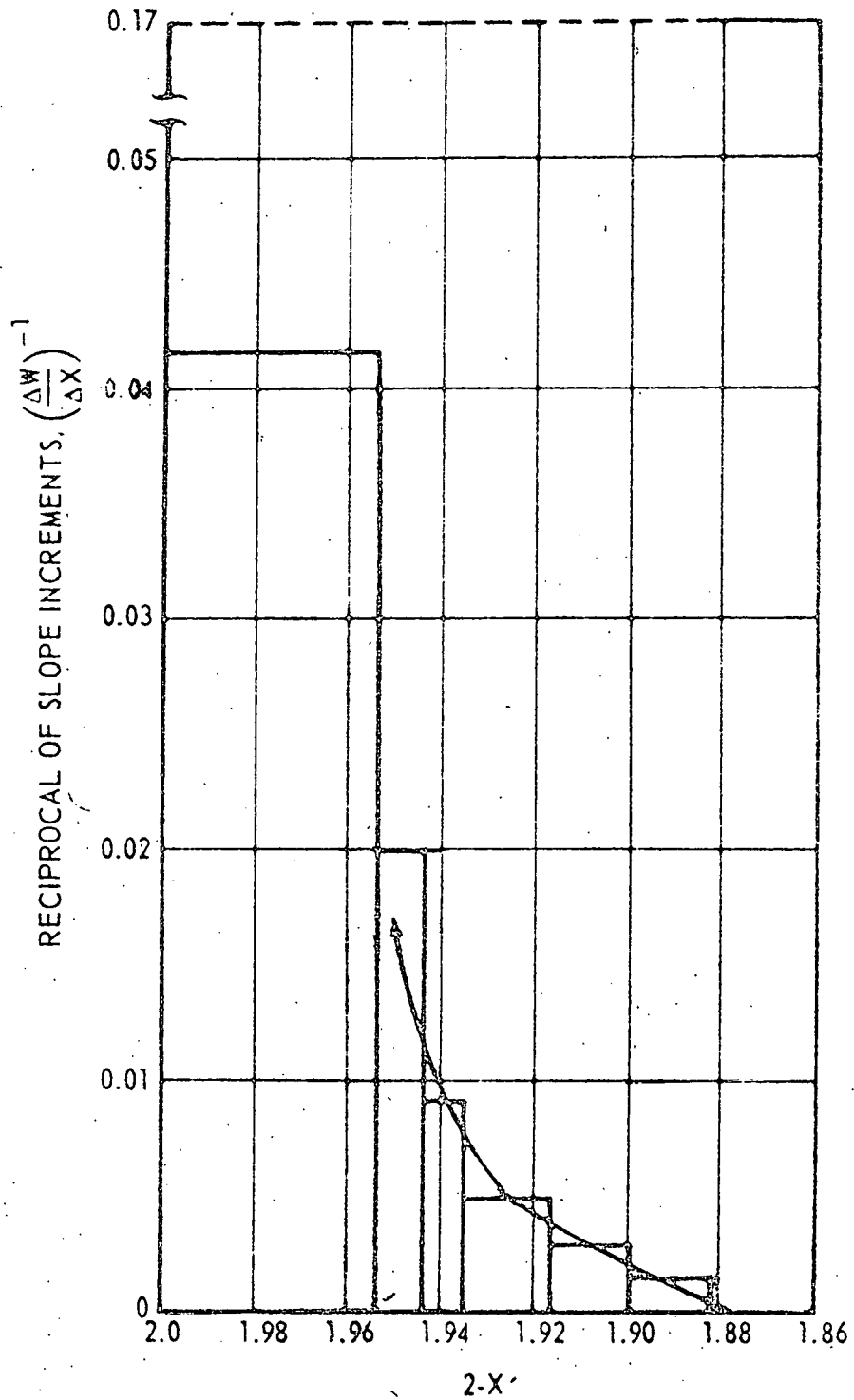


FIGURE 3

confirmed by direct observation. Indirect evidence, however, has been obtained that there is no uranium metal present in  $\text{UO}_2\text{-x}$  ( $x < 0.11$ ) 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  $\text{UO}_2$  pellet above  $2200^\circ\text{C}$  showed very rapid melting and attack of the rhenium wire.

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