Report No. BMI-1175
Chemistry
(TID-4500, 12th Ed.)

I

Contract No. W-7405-eng-92

EXPERIMENTS ON THE PREPARATION OF UO_{2-x} AND UO

by

Dale A. Vaughan
Carl W. Melton
Arnold F. Gerds

March 6, 1957

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

II

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
EXPERIMENTAL WORK AND RESULTS	1
Substoichiometric UO_2	2
Uranium Monoxide	3
Reacting Uranium With Higher Oxides	3
Reacting Mixed-Powder Compacts of UC and UO_2	3
Properties of U(C,O)	8
Hardness	8
Corrosion Resistance	8
DISCUSSION OF RESULTS	8
REFERENCES	10

1

EXPERIMENTS ON THE PREPARATION OF UO_{2-x} AND UO

Dale A. Vaughan, Carl W. Melton, and Arnold F. Gerds

BMI-1175

Reactions designed to reduce the oxygen content of UO_2 below stoichiometric composition are described. No evidence was found for the existence of substoichiometric UO_2 . The reaction of metal with $\text{UO}_2 + x$ yields a phase described in the literature as uranium monoxide, UO . However, the reaction proceeds at a low rate and the reaction products are contaminated with a large amount of UO_2 . The reaction of UC with UO_2 is described: this reaction is capable of producing a single-phase material of composition $\text{UC}_x\text{O}_{1-x}$ ($x \approx 0.5$) by heating in vacuum at 1600 to 1800 C.

INTRODUCTION

The existence of two uranium oxides with an oxygen-uranium ratio less than 2 has been reported⁽¹⁾, one having the UO_2 (fluorite) structure, but containing less than the stoichiometric oxygen content, and the second having the NaCl structure with the composition UO . However, some controversy over the existence of lower oxides has resulted from the inability to prepare them in bulk quantities.

Studies of the uranium-oxygen system prior to 1951 were reviewed by Katz⁽¹⁾. Subsequently, Perio⁽²⁾ studied the reaction between UO_2 and uranium at 500 C. His results agreed with those of Zachariasen as reported by Katz⁽¹⁾ that an oxide having a UO_2 structure with a range of oxygen content below stoichiometric existed. In the present investigation, this reaction has been reinvestigated, and the temperature range extended to the melting point of UO_2 .

Uranium monoxide, UO , has never been prepared in bulk quantities. Evidence for its existence was based upon X-ray diffraction data obtained from thin surface films on uranium metal heated in vacuum, as reported by Katz, and from metallographic evidence on microconstituents in ingot uranium obtained at Battelle⁽³⁾. Earlier at Battelle, similar X-ray results were obtained when uranium carbide was exposed to a low partial pressure of oxygen at high temperature. In the present study, two methods for preparing bulk quantities of UO were investigated, (1) heating uranium in a low partial pressure of oxygen, and (2) reacting UC with UO_2 .

EXPERIMENTAL WORK AND RESULTS

The controversy that is found in the literature^(1,2) on the existence of the oxides of uranium lower than UO_2 might be resolved if a reliable method of oxygen analysis was known. Ignition analysis, in which the sample is fired to U_3O_8 , is of doubtful value in this case, since it does not detect the possible presence of a second phase,

(1) References at end of report.

such as free metal. However, the lattice parameter of $\text{UO}_{2.00}$ (5.472 Å) decreases with excess oxygen and would be expected to increase for substoichiometric oxide. This assumption is based on the general effect of valence on metal-ion radius. In the present investigation, therefore, the lattice-parameter measurements were used to determine the oxygen content of the oxide phase. Metallographic techniques in conjunction with X-ray diffraction and carbon analysis were employed in the identification of UO. The staining characteristics of UO, UC, and UN, described in a previous report⁽³⁾, were employed in the present investigation. Lattice-parameter measurements were made and compared with those reported⁽³⁾ for UC (4.961 Å), UO (4.920 Å), and UN (4.890 Å). The carbon analyses were made by burning the oxides in oxygen and absorbing the resulting CO_2 in an Ascarite gravimetric train.

Substoichiometric UO_2

The most recent work of Perio⁽²⁾ indicates that partial reduction of UO_2 can be attained by reacting metallic uranium and UO_2 at 500 C. The procedure outlined by Perio was repeated in the present work. Pellets, containing $\text{UO}_{2.04}$ and 25 or 50 a/o uranium, were heated for 1 to 5 days at 500 C in vacuum. The lattice parameter of the UO_2 phase increased from 5.468 to 5.472 Å, suggesting a decrease in the oxygen content to $\text{UO}_{2.00}$. Higher temperature heat treatments (800 to 1000 C) gave the same results. Arc melts were made of UO_2 containing 50 a/o uranium. The resulting ingots were examined metallographically. Dendrites of UO_2 in a uranium matrix were observed, but there was no evidence of UO at the interface. The UO_2 lattice parameter corresponded to that of stoichiometric oxide. Heating the ingots for 500 hr at temperatures up to 1000 C did not produce a change in the phases observed. These results suggested that the oxygen-uranium ratio in UO_2 could not be reduced below 2 by reaction with the metal. The oxygen-uranium ratio of the reacted mixtures could not be analyzed chemically, because all of the samples contained the two phases, uranium and UO_2 .

Oxidation of uranium in a 316 C steam autoclave was reported⁽⁴⁾ to yield UO_{2-x} . During the present investigation an attempt was made to repeat this work. The results of this work, given in Table 1, show no evidence for a UO_{2-x} phase. Sample 44A, which analyzed by ignition $\text{UO}_{1.08}$, gave UH_3 and UO_2 by X-ray diffraction. The other samples gave only the UO_2 pattern; the patterns were extremely diffuse and could not be used for lattice-parameter determinations. Subsequently, Sample 42A was annealed in a sealed silica capsule for 4 hr at 600 C and reanalyzed. This sharpened the X-ray pattern. A slight increase in the oxygen-uranium ratio to 1.96 resulted. However, the lattice constant of the annealed oxide was found to be 5.4710 Å, corresponding to that of $\text{UO}_{2.01}$, so it would appear that a small amount of uranium metal or UH_3 remained in the sample.

TABLE 1. STEAM OXIDATION OF URANIUM

Sample	Oxidation		Oxygen-Uranium Ratio	Phases Identified By X-Ray Diffraction
	Time, hr	Temperature, C		
42A	2	300	$\text{UO}_{1.95}$	UO_2
44A	1/2	300	$\text{UO}_{1.08}$	$\text{UO}_2 + \text{UH}_3$
45A	1	300	$\text{UO}_{2.11}$	UO_2
46A	4	300	$\text{UO}_{1.98}$	UO_2

Uranium Monoxide

Reacting Uranium With Higher Oxides

As reported in the previous section, the results of the present study of the uranium- $\text{UO}_{2.0}$ reaction indicate that UO_2 cannot be reduced to a substoichiometric composition by heating at temperatures from 500 C to the melting point of UO_2 , approximately 2700 C. However, oxides containing more than 2 atoms of oxygen per atom of uranium are reduced more readily. Experiments were carried out to determine if bulk quantities of UO could be prepared by reacting wafers of metal with UO_{2+x} oxides, in vacuum and in argon. Wafers of metal 1/16 to 1/8 in. thick were reacted with $\text{UO}_{2.4}$ and $\text{UO}_{2.66}$ at 1850 C and 1600 C, respectively, for 6 to 9 hr. X-ray diffraction and metallographic examination of the wafers showed a thin surface layer consisting of UO_2 and a UO -like phase; however, the core had not reacted. The oxide immediately around the wafer changed color from black to red ($\text{UO}_{2.00}$ is brick red). Owing to the slow diffusion of oxygen into the wafer and the high percentage of UO_2 in the reaction product, this method of preparation of UO was discontinued.

Reacting Mixed-Powder Compacts of UC and UO_2

A second method used to produce material having the structure of UO was the reaction of intimately mixed compacted powders of UC and UO_2 in vacuum at elevated temperatures. Results of some experiments using this procedure are summarized in Table 2. This table also lists the phases identified by X-ray diffraction and metallographic techniques.

It is apparent that only a slightly larger yield of a phase having the appearance of UO was obtained when the ratio of UC to UO_2 was changed from 1 to 2 to 1 to 1, as shown in Figure 1. A marked increase in the amount of this phase was obtained in a UC- UO_2 sample, having a ratio of 2-1/2 to 1, heated at 1800 C for 2 hr in vacuum. The microstructure of this sample, shown in Figure 2, appears to contain about 70 to 80 per cent of the UO -like phase.

Metallic uranium containing UC as a dendritic phase was produced on the surfaces of all of the compacts during reaction. As the ratio of UC to UO_2 was increased, more metallic uranium was formed. The amount of metal produced also appeared to increase with increasing temperature above 1600 C.

Attempts were made to produce UO or to increase the yield of the light-colored UO -like phase by multiple heatings of the compacted powder mixtures. Between heatings, the compacts were crushed, sieved through a 325-mesh screen, and recompact. A four-stage heating cycle, which included a 1/2-hr treatment at 1600 C in hydrogen, yielded a very high proportion of the light-colored phase. This microstructure is shown in Figure 3 at two magnifications. Perhaps the brief heating in hydrogen contributed to the increased yield in this experiment.

X-ray diffraction examination of the several samples described in Table 2 revealed a range of lattice parameters from 4.958 to 4.9488 Å, for the phase identified metallographically as UO . This range was ascribed to differences in the amount of oxygen in the UC structure after reacting with UO_2 for various times and temperatures.

TABLE 2. SUMMARY OF ATTEMPT TO PREPARE URANIUM MONOXIDE BY REACTION OF COMPACTED POWDER MIXTURES OF UC AND UO_2

Sample	UC- UO_2 Ratio	Initial Carbon, w/o	Reaction		Microstructure			Reaction Product		
			Temperature, C	Time, hr	Phases	Estimated UO_2 , per cent	Figure	Phases Determined by X-Ray	Lattice Parameter of U(C, O) Phase, A	Carbon, w/o
UO-10	1/2	1.5	1800	2-1/2	$\text{UO}_2 + \text{UO}$	20-30	1	$\text{UO}_2 + \text{U(C, O)}$	4.9488	1.22
UO-14	1/1.5	1.8	1700	2-1/2	$\text{UO}_2 + \text{UO}$	20-30	2	$\text{UO}_2 + \text{U(C, O)}$	4.9505	1.46
UO-15	1/1	2.2	1700	2-1/2	$\text{UO}_2 + \text{UO}$	20-30	3			
UO-22	2.5/1	3.3	1800	2	$\text{UO} + \text{UO}_2$	70-80	4	$\text{U(C, O)} + \text{UO}_2$	4.9538	
UO-23	2.5/1	3.3	(a)		$\text{UO} + \text{UO}_2$			$\text{U(C, O)} + \text{UO}_2$	4.9581	2.3
UO-25	2/1	3.1	(b)		$\text{UO} + \text{UO}_2$	60-70	5	$\text{U(C, O)} + \text{UO}_2$	4.9515	1.6
UO-21	2.5/1	3.3	(c)		$\text{UO} + \text{UO}_2$	90	6+7	$\text{U(C, O)} + \text{UO}_2$	4.9490	2.7

(a) Heated at 1600 C for 2 hr in vacuum, crushed, recompact, and heated at 1800 C for 1 hr in vacuum.

(b) Heated at 1800 C for 2 hr in vacuum, crushed, recompact, and heated at 1800 C for 2 hr in vacuum.

(c) Heated at 1600 C for 2 hr in vacuum, 1600 C for 2 hr in vacuum, 1600 C for 1/2 hr in hydrogen and 1/2 hr in vacuum, and 1800 C for 2 hr in vacuum. The pellet was crushed and recompact between heatings.

5

100X

N27511

Sample UO-10; 2 Parts UO_2 to 1 Part UO ,
Heated 2-1/2 Hr at 1800 C in Vacuum

100X

N27519

Sample UO-14; 1-1/2 Parts UO_2 to 1 Part UO ,
Heated 2-1/2 Hr at 1700 C in Vacuum

100X

N27805

Sample UO-15; 1 Part UO_2 to 1 Part UC ,
Heated 2-1/2 Hr at 1700 C in Vacuum

FIGURE 1. EFFECT OF UC-UO_2 RATIO ON THE AMOUNT OF REACTION PRODUCT

The gray phase is UO_2 . The light etching phase has the UO structure.
The etchant was composed of equal volumes of nitric acid, acetic acid, and water.

5

100X

N31341

Sample UO-22; 1 Part UO_2 to 2-1/2 Parts UC, heated 2 Hr at 1800 C in Vacuum

100X

N31919

Sample UO-25A; 1 Part UO_2 to 2-1/2 Parts UC, Heated 2 Hr at 1800 C in Vacuum;
Recrushed, Recompactd, and Heat Treatment Repeated

FIGURE 2. EFFECT OF TIME AT TEMPERATURE ON AMOUNT OF REACTION PRODUCT

Light-colored phase is UO and gray phase is UO_2 .

100X

N31343

250X

N31344

FIGURE 3. EFFECT OF MULTIPLE HEATINGS ON THE AMOUNT OF REACTION PRODUCT

Reaction approximately 90 per cent completed. Sample UO-21C, 2-1/2 parts of UC to 1 part of UO_2 , heated in four stages at 1600 and 1800 C in vacuum and hydrogen. Gray phase is UO_2 , light phase is UO matrix.

The lattice parameters reported are to be compared with 4.961 Å, the lattice parameter of UC. Carbon analyses on selected samples are listed in the last column of Table 2. These analyses indicate that the reacted compacts did retain appreciable carbon. Etching tests on the products of the reactions failed to show any evidence of UC in the microstructures. Also no phase was noted which could be identified as free carbon. This indicated that the light-colored phase actually is not UO but rather a three-component phase of the form UC_xO_{1-x} . Such a compound consists of a solid solution of oxygen in UC, in which oxygen replaces carbon in the lattice. Since some carbon was used in forming a thin layer of metallic uranium, and since the reactions were incomplete, the carbon assays given in the last column of Table 2 cannot be compared directly with the lattice parameter of the U(C,O) phase. However, in the case of Sample UO-21, only the center of the pellet was analyzed. The analysis and lattice parameter were in close agreement with values calculated for complete conversion of the 2.5 UC-UO₂ ratio to U(C_{0.57}O_{0.43}) plus CO.

Properties of U(C,O)

Hardness

Hardness measurements using the Tukon tester were made on some of the larger particles of U(C,O) produced. Results of these tests are summarized in Table 3. All of the hardness measurements were made with a 100-gram load on the Knoop indenter. Although heavier loads would have been more desirable, the size of the individual particles would not permit larger indentations.

These measurements indicate that the U(C,O) phase has a Knoop hardness between about 1000 and 1050. This compares with a value of 200 to 350 for the uranium. Similar hardnesses obtained on a sample of the very brittle UC showed Knoop values of about 750. However, because of the brittle nature of UC, this average value must be considered a minimum hardness. Thus, it appears that UO containing between 1 and 2.5 w/o carbon may be at least as hard or slightly harder than UC.

Corrosion Resistance

Portions of Samples UO-25 and UO-21 of Table 2, and samples of stoichiometric UC, were exposed to boiling water and to hot and cold acids to determine their resistance to attack. The results are shown in Table 4. UC was attacked more rapidly than U(C,O) on exposure to boiling water, the reverse being true in concentrated nitric acid at room temperature. Little or no difference in attack was observed on exposure to dilute nitric acid or to HCl.

DISCUSSION OF RESULTS

Differing results have been reported in the literature as to the existence of UO₂ with less than stoichiometric oxygen content. In contrast to the most recent report by Perio⁽²⁾, the present investigation indicates that the reduction cannot be accomplished by reacting UO₂ with metal at temperatures from 500 to 2700 C.

TABLE 3. KNOOP HARDNESS OF U(C,O) COMPARED WITH THAT OF URANIUM

Sample	History	Knoop Hardness (100-G Load)		Phase
		Individual Determinations	Average	
UO-10	1 part of UC mixed with 2 parts of UO ₂ , compacted and heated at 1800 C for 2 hr in vacuum	1051 1051 951	1017	U(C,O)
UO-14	1 part UC mixed with 2 parts UO ₂ powder, compacted and heated at 1700 C for 2-1/2 hr in vacuum	996 1051 1075 975	1024	U(C,O)
UO-4	Uranium melted with U ₃ O ₈ powder and heated rapidly to about 1500 C in argon	352 356 328 378	353	Uranium metal
UO-25	Heated at 1800 C for 2 hr in vacuum, crushed, recompact, and heat treatment repeated	1098 1023 975	1032	U(C,O)
UO-25	Heated at 1800 C for 2 hr in vacuum, crushed, recompact, and heat treatment repeated	118 180 190 282 143 342	209	Uranium metal

TABLE 4. COMPARISON OF REACTIVITIES OF UC AND U(C,O) IN VARIOUS CORROSION MEDIA

Corrosion Medium and Temperature	Apparent Reaction Rates	
	UC	U(C,O)
Boiling tap H ₂ O	Rapid	Slow
Boiling deionized H ₂ O	Rapid	Slow
RT concentrated HNO ₃	Very slow(a)	Rapid
RT 1 N HNO ₃	No reaction	No reaction
Boiling 1 N HNO ₃ (b)	Slow	Slow
RT concentrated HCl	Very slow	Very slow
Boiling concentrated HCl	Very slow	Very slow

(a) A black film forms, after which the reaction appears to stop.

(b) As boiling increased the HNO₃ concentration, the UC formed a black film and the reaction stopped, while the U(C,O) dissolved completely.

Although a phase identified as UO has been cited in the literature, bulk quantities have not been obtained in the pure form. Reaction of higher oxides with metal have produced thin surface layers of a UO-like phase. However, the reaction is slow even at 1800 C, and the product is contaminated with large amounts of UO₂. The reaction between UC and UO₂, producing UC_xO_(1-x) plus CO, goes nearly to completion when carried out in vacuum at 1600 to 1800 C. The value of x depends upon the proportion of UC and UO₂ used. In the present work, completion of the reaction $UC + 2UO_2 \rightarrow 3UO + CO$ was not attained, but with reactant mixtures of higher UC-UO₂ ratios, a nearly single-phase material of the composition U(C,O) was produced. A decrease in lattice parameter of UC, consistent with partial replacement of the carbon in the UC lattice with oxygen, was observed. If the reaction of 2.5 UC with 1 UO₂ were carried to completion, one would expect 43 per cent of the carbon to be replaced with oxygen. Assuming that Vegard's law is obeyed, this substitution would decrease the lattice parameter of UC from 4.961 Å to 4.945 Å. Sample UO-21 of Table 2, which was approximately 90 per cent reacted, gave a lattice parameter of 4.949 Å. Correcting for the unreacted portion, this sample showed good agreement with the calculated carbon content.

REFERENCES

- (1) Katz, J., and Rabinowitz, E., The Chemistry of Uranium, McGraw-Hill Book Company, Inc., New York (1951).
- (2) Perio, P., Bulletin de Societe Chimique de France, 351 (1952).
- (3) Dickerson, R. F., Gerds, A. F., and Vaughan, D. A., Journal of Metals, 8, 456-460 (April, 1956).
- (4) Shapiro, Z. M., WAPD, private communication.

DAV:CWM:AFG/mmk