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COMPARISON OF ACTIVE AND INACTIVE URANIUM
DIOXIDE-OXYGEN SYSTEMS

by

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COMPARISON OF ACTIVE AND INACTIVE URANIUM DIOXIDE-OXYGEN SYSTEMS

Dale A. Vaughan, J. Robert Bridge, and Charles M. Schwartz

Inactive UO_2 oxidizes at 180 C by the formation of a tetragonal oxide (U_3O_7), which is unstable, on heating above 300 C. The U_3O_7 in compositions below $\text{UO}_{2.25}$ reacts with UO_2 to form UO_{2+x} and U_4O_9 . At compositions above $\text{UO}_{2.25}$, the tetragonal phase is stable to 600 C. In the homogenized condition, both U_3O_7 and U_4O_9 are n-type conductors, while UO_{2+x} is p-type. The solubility limit of oxygen in UO_2 , as determined by X-ray diffraction data and electrical measurements, is $\text{UO}_{2.08}$ at 25 and 200 C, $\text{UO}_{2.11}$ at 400 C, $\text{UO}_{2.17}$ at 600 C, and $\text{UO}_{2.20}$ above 700 C. The active UO_2 oxidation product retains the cubic symmetry of UO_2 up to the composition $\text{UO}_{2.40}$ and is stable to 600 C in vacuum. The structural behavior of the active oxide in this composition range is significantly different from that of the inactive oxide.

INTRODUCTION

The phase compositions in the UO_2 -oxygen system have received considerable attention since 1950. Although the several phases UO_2 , U_4O_9 , U_3O_7 , U_2O_5 , and U_3O_8 had been previously established and reported by Katz and Rabinowitch⁽¹⁾, the extent of the solid solubilities, the stability of the several phases, and the oxidation mechanism of UO_2 have been the subjects of several papers in recent years. Gronvold⁽²⁾ was the first to report X-ray diffraction data on the uranium-oxygen system at elevated temperatures. His results show little or no solid solubility of oxygen in UO_2 below 250 C but a rapid increase in oxygen solubility above this temperature. On the other hand, Perio⁽³⁾, who used room-temperature X-ray data, indicated no solubility of oxygen in UO_2 ; rather, he claimed that cubic UO_{2+x} is metastable in relation to mixtures of UO_2 and U_4O_9 . The phase composition between U_4O_9 and U_3O_8 has received considerable attention by Perio⁽³⁾ and Anderson⁽⁴⁾. They reported a number of tetragonal phases in this region by low-temperature oxidation of UO_2 and that these oxides are metastable with respect to U_4O_9 and U_3O_8 . The decomposition of the tetragonal oxides appears to occur stepwise. Although these oxides are metastable, they are of considerable importance to the understanding of the mechanism of oxidation of UO_2 . The authors⁽⁵⁾ of this report observed that preparations of UO_2 which oxidize rapidly to $\text{UO}_{2.4}$ at room temperature retain the cubic symmetry of UO_2 .⁽⁵⁾ Perio⁽⁶⁾ also observed a cubic oxide for a composition of $\text{UO}_{2.35}$ and suggested that this cubic structure was stable to 300 C.

The present investigation was carried out to obtain additional data on the solid solubility limit in UO_2 and to obtain additional information on the stability of the oxide phases between U_4O_9 and U_3O_8 . Since differences in the chemical reactivity (as measured by rates of reoxidation or of hydrofluorination of UO_2) were previously observed⁽⁵⁾, it was of interest to determine if the reactivity could be related to the structural properties of active and inactive oxide.

(1) References at end.

EXPERIMENTAL WORK

The uranium dioxide used in this investigation was obtained in the inactive form from Mallinckrodt Chemical Works. Active oxide was prepared in the laboratory by hydrogen reduction of amorphous UO_3 , as described previously⁽⁵⁾. Inactive oxide with oxygen content higher than $\text{UO}_{2.01}$ was made by oxidizing the Mallinckrodt oxide in dry oxygen at 180 C. The oxygen-to-uranium ratio of various preparations, as a function of time at 180 C, is shown in Figure 1. The upper curve of Figure 1 indicates that moisture in tank oxygen accelerates the oxidation. Active oxide oxidized rapidly when handled in air at room temperature. Several different compositions in the range $\text{UO}_{2.14}$ to $\text{UO}_{2.41}$ were obtained from various preparations, as shown in Table 1. The oxygen content of all samples was obtained by weight-gain measurements upon ignition to U_3O_8 at 750 C.

X-ray diffraction data at room and elevated temperatures were obtained on the as-made oxides and on oxides homogenized for 100 hr at 450 C. During homogenization, the oxides were sealed in evacuated capsules. The oxygen-to-uranium ratio of the homogenized oxide was redetermined before the oxide was loaded into thin-walled quartz capillaries for high-temperature X-ray diffraction studies.

The electrical properties of the oxide preparations described above were determined on samples hydrostatically pressed at 100,000 psi (without a binder) into cylindrical rods about 1/4 by 4 in. from which individual specimens were cut and shaped to 1/8 by 1/4 by 1/2 in. Conductivity, thermoelectric power, and carrier-type determinations were made of the as-oxidized samples and after homogenizing at 200 C and 400 C.

RESULTS

Inactive Oxide

X-ray diffraction data obtained from samples over the range of oxygen contents $\text{UO}_{2.01}$ to $\text{UO}_{2.32}$ are shown in Table 2. The intensity of the UO_2 pattern of as-made oxides decreases with increasing oxygen content. The oxidation phase, which has a tetragonal structure, was first detected at the composition $\text{UO}_{2.07}$. Its pattern consists of broad diffraction lines that do not sharpen appreciably until the samples are homogenized at 450 C. During homogenization, the tetragonal phase disappears from compositions below $\text{UO}_{2.26}$ and a second cubic phase, U_4O_9 , is formed. As shown in Table 2, this cubic oxide coexists with UO_2 for oxygen-to-uranium ratios from 2.12 to 2.24 and with the tetragonal U_3O_7 phase from $\text{UO}_{2.26}$ to $\text{U}_2.32$. High-temperature X-ray diffraction examination showed the reaction $\text{U}_3\text{O}_7 + \text{UO}_2 \rightarrow \text{UO}_{2+x} + \text{U}_4\text{O}_9$ to go to the right on heating the samples to 300 C. An attempt to convert the U_4O_9 structure back to tetragonal U_3O_7 by heating for 200 hours at 120 C was not successful.

The thermal expansion of UO_{2+x} is seen (Figure 2) to be approximately linear ($\alpha = 9.9 \times 10^{-6}$) from 25 to 800 C. The oxide $\text{UO}_{2.16}$ is two phases, UO_{2+x} and U_4O_9 , from 25 to 400 C, and single-phase UO_{2+x} above 500 C. The increasing solubility of

FIGURE 1. OXIDATION OF INACTIVE OXIDE IN OXYGEN AT 180 C

TABLE 1. METHOD OF PREPARATION AND OXYGEN-TO-URANIUM
RATIOS OF SEVERAL SAMPLES OF ACTIVE UO_2

UO_3 Denitration Process	UO_3 , per cent	Reduction Method	Oxygen-to-Uranium Ratio After Exposure to Air
UNH vacuum dried at 150 C then denitrated at 300 C for 4 hr		Tank hydrogen 2 hr at 600 C, flushed with argon and oxygen at 25 C	2.41
Ditto		Tank hydrogen 2 hr at 600 C, flushed with argon and nitrogen at 25 C	2.19
UNH vacuum dried at 150 C then denitrated at 400 C for 4 hr	99.5	Dry hydrogen 2 hr at 600 C, exposed to air at 25 C	2.41
UNH vacuum dried at 150 C then denitrated at 300 C for 4 hr	98.9	Dry hydrogen 2 hr at 600 C, exposed to air at 25 C	2.30
UNH dried and denitrated in a thin bed 1/2 hr at 450 C	98.5	Dry hydrogen 2 hr at 600 C, exposed to oxygen then air at 25 C	2.38
Ditto	98.6	Water-saturated hydrogen 2 hr at 600 C, then exposed to air at 25 C	2.14
"	98.5	Water-saturated hydrogen 2 hr at 600 C, then exposed to nitrogen and air at 25 C	2.25

TABLE 2. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF AS-OXIDIZED AND HOMOGENIZED MALLINCKRODT UO_2

As Oxidized at 180 C		Oxides Homogenized at 450 C	
Oxygen-to-Uranium Ratio	Phases Identified ^(a)	Oxygen-to-Uranium Ratio	Phases Identified
2.01	UO_{2+x} ^(b)		
2.03	UO_{2+x} (as received)		
2.05	UO_{2+x}	2.05	UO_{2+x}
2.07	$\text{UO}_{2+x} + \text{VVF-U}_3\text{O}_7$	2.07	UO_{2+x}
2.11	$\text{UO}_{2+x} + \text{VVF-U}_3\text{O}_7$		
2.12	$\text{UO}_{2+x} + \text{VVF-U}_3\text{O}_7$	2.12	$\text{UO}_{2+x} + \text{VVF-U}_4\text{O}_9$
2.13	$\text{UO}_{2+x} + \text{VF-U}_3\text{O}_7$	2.14	$\text{UO}_{2+x} + \text{F-U}_4\text{O}_9$
2.14	$\text{UO}_{2+x} + \text{VF-U}_3\text{O}_7$	2.12	$\text{UO}_{2+x} + \text{VVF-U}_4\text{O}_9$
2.16	$\text{UO}_{2+x} + \text{VF-U}_3\text{O}_7$		
2.19	$\text{UO}_{2+x} + \text{F-U}_3\text{O}_7$	2.19	$\text{UO}_{2+x} + \text{S-U}_4\text{O}_9$
2.21	$\text{UO}_{2+x} + \text{F-U}_3\text{O}_7$	2.24	$\text{UO}_{2+x} + \text{VS-U}_4\text{O}_9$
2.26	$\text{UO}_{2+x} + \text{M-U}_3\text{O}_7$	2.28	
2.27	$\text{UO}_{2+x} + \text{M-U}_3\text{O}_7$	2.26	$\text{U}_4\text{O}_9 + \text{F-U}_3\text{O}_7$
2.29	$\text{UO}_{2+x} + \text{MS-U}_3\text{O}_7$	2.29	$\text{U}_4\text{O}_9 + \text{S-U}_3\text{O}_7$
2.32	$\text{UO}_{2+x} + \text{S-U}_3\text{O}_7$	2.32	$\text{U}_4\text{O}_9 (?) + \text{VS-U}_3\text{O}_7$

(a) The lattice parameter of the UO_{2+x} phase at room temperature decreased approximately 0.002 Å during these oxidation treatments.

(b) Mallinckrodt UO_2 hydrogen treated at 1000 C.

FIGURE 2. UNIT-CELL DIMENSIONS VERSUS TEMPERATURE FOR INACTIVE UO_2

U_4O_9 in UO_{2+x} between 300 and 500 C causes a marked deviation from linearity in the thermal expansion of this sample. However, in the case of the U_4O_9 , the expansion of the unit cell deviates appreciably from linearity in the 25 to 300 C temperature range, with a linear expansion ($\alpha = 11.8 \times 10^{-6}$) above 300 C. The unit-cell size of the U_4O_9 phase is slightly greater for compositions below $\text{UO}_{2.25}$ than it is for compositions above $\text{UO}_{2.25}$. This suggests a small variation in composition within the narrow U_4O_9 single-phase field. The change in the cell dimensions of the tetragonal U_3O_7 structure from 25 to 600 C is shown in Figure 3. There was no evidence obtained for a change in the structure of U_3O_7 over this temperature range.

The phase boundary between UO_{2+x} and UO_{2+x} plus U_4O_9 was established as shown in Figure 4 by isothermal plots at 25, 200, 400, 600, and 800 C of lattice parameters of the cubic phases UO_{2+x} and U_4O_9 versus the oxygen-to-uranium ratio. Consistent results were observed by the parametric method and by the disappearing-phase method, thus indicating the oxygen solid solubility limit in UO_2 to be $\text{UO}_{2.08}$ at 25 and 200 C, increasing to $\text{UO}_{2.11}$ at 400 C, to $\text{UO}_{2.17}$ at 600 C, and $\text{UO}_{2.20}$ above 700 C. Lattice parameters of UO_{2+x} , U_4O_9 , and U_3O_7 versus temperature, for various oxygen-to-uranium ratios, are given in Table 3.

It is difficult to understand the existence of the two phases UO_{2+x} and U_4O_9 which have such similar structures with less than 1 per cent difference in cell size. Electrical properties were determined on portions of the sample used in the X-ray diffraction investigation to aid in interpreting the X-ray results.

Room-temperature measurements on the as-prepared specimens revealed that all compositions were *p*-type and that the conductivity increased but very little with oxygen content. This would suggest that very little oxygen entered the UO_2 lattice and that the oxidation product has a low carrier concentration of the metal-deficit or oxygen-excess *n*-type. These results are consistent with X-ray results which showed a very small decrease in lattice constant of the UO_2 phase as oxidation progressed at 180 C and that the tetragonal oxidation product was difficult to further oxidize at 180 C.

In view of the changes in structure that were observed by X-ray diffraction during homogenization, the electrical properties were determined on samples homogenized and quenched from 200 and 400 C. The progressive change in electrical conductivity during homogenization is shown in Figures 5 and 6 for a range of oxygen-to-uranium ratios. Since the carrier concentration, as determined by the magnitude of the conductivity, decreases with increasing oxygen content between $\text{UO}_{2.08}$ and $\text{UO}_{2.13}$ and the carrier type changes from *p*- to *n*-type above $\text{UO}_{2.13}$, distinct differences in structure are suggested and verify the X-ray diffraction results. Also, the marked drop in conductivity between $\text{UO}_{2.26}$ and $\text{UO}_{2.32}$ can be interpreted as a phase change. It is interesting to note that the oxide with a composition slightly greater than U_4O_9 has *n*-type carriers. This would suggest that the stoichiometric compound U_4O_9 does not exist but always contains a donor excess. One cannot determine on the basis of carrier type whether the *p*-type conductivity of the oxide is due to a metal excess or an oxygen deficient structure or, in the case of *p*-type conductivity, whether the structure contains an excess of oxygen or a deficiency of metal atoms. Thus, one must combine interstitial hole size, ion size, and valence considerations with the electrical properties to determine the exact mechanism of conduction and the reason for the existence of the two-phase region of the oxides UO_{2+x} and U_4O_9 , which have such small differences in structure.

FIGURE 3. UNIT-CELL DIMENSIONS OF U_3O_7 VERSUS TEMPERATURE

FIGURE 4. ISOTHERMAL CELL SIZE VERSUS OXYGEN CONTENT OF INACTIVE OXIDES UO_{2+x} AND U_4O_9

TABLE 3. UNIT-CELL DIMENSIONS OF THE INACTIVE UO_2 -OXYGEN SYSTEM

Temperature, C	Cell Dimension, A										(b)	Two-Phase U ₄ O ₉ + U ₃ O ₇ ^(c)		U ₃ O ₇ Phase Field
	UO _{2+x} Phase Field			Two-Phase UO _{2+x} + U ₄ O ₉ ^(a)						UO _{2.27}		UO _{2.29}	UO _{2.32}	
	UO _{2.01}	UO _{2.05}	UO _{2.07}	UO _{2.12}	UO _{2.14}	UO _{2.16}	UO _{2.19}	UO _{2.21}	UO _{2.24}					
25	5.4708	5.4675	5.4662	5.4646	5.4654 5.4434	5.4638 5.4434	5.463 5.4439	5.4430	5.4431		5.4402		a = 5.408 c = 5.504	
100				5.4704										
200	5.4794	5.4775	5.4742		5.4727 5.4457	5.4740	5.4721 5.4477	5.4478	5.4465		5.4453	5.444	a = 5.418 c = 5.486	
300			5.4820	5.4800	5.4808 5.4535	5.4797 5.4513		5.4531	5.4502		5.4497			
400	5.4892	5.4875	5.4874	5.4821	5.4836 5.4594	5.4815 5.4565	5.4819 5.4579		5.4571		5.4557	5.4551	a = 5.433 c = 5.505	
500				5.4881	5.4878	5.4864		5.4663	5.4638		5.4614		a = 5.436 c = 5.512	
600	5.5010	5.4992	5.4993	5.4938	5.4938	5.4914		5.4717	5.4703		5.4674	5.4682	a = 5.450 c = 5.508	
700						5.4959					5.4754			
800	5.5129	5.5114					5.4978					5.4820		

(a) The lattice parameter of only one phase was measured near the boundaries.

(b) No single phase sample of U_4O_9 was prepared.(c) The lattice parameters of the U_3O_7 phase were not determined in this two-phase field.

FIGURE 5. CHANGE OF CONDUCTIVITY WITH ANNEAL TIME AT 200 C FOR PRESSED SPECIMENS OF UO_2 OF VARIOUS OXYGEN-TO-URANIUM RATIOS

FIGURE 6. CHANGE OF CONDUCTIVITY WITH ANNEAL TIME AT 400 C FOR PRESSED SPECIMENS OF UO_2 OF VARIOUS OXYGEN-TO-URANIUM RATIOS

Active Oxide

In comparing active UO_2 with inactive UO_2 , only the structural relationships have been investigated. The study of active preparations of uranium dioxide has been limited to compositions between $\text{UO}_{2.14}$ and $\text{UO}_{2.43}$ because the rapid oxidation of active UO_2 on exposure to air or oxygen at room temperature prevented obtaining samples closer to the stoichiometric value. X-ray diffraction data were obtained for compositions and temperatures as shown graphically in Figure 7. The tabulated data are in Table 4. For compositions below $\text{UO}_{2.25}$ the active UO_2 -oxygen system is essentially the same as the inactive UO_2 -oxygen system as far as the data permit comparison. However, for compositions greater than $\text{UO}_{2.25}$ a distinct difference in behavior between the active and inactive oxide was observed, namely, that the oxidation phase retains cubic symmetry rather than forming the tetragonal U_3O_7 phase as did the inactive oxide. The cubic oxidation product of the active oxide is differentiated from U_4O_9 by a smaller room-temperature cell size. Both the tetragonal U_3O_7 and the cubic oxide exhibit linear thermal expansion from room temperature to 600 C. The electrical properties of the active oxides have not been determined. Attempts to measure conductivity of this material were not reliable due to instabilities in the material. This instability could be interpreted as a lack of bonding of the excess oxygen in the structure.

CONCLUSIONS

Structural studies of the UO_2 -oxygen systems for active and inactive UO_2 revealed little or no difference for compositions below $\text{UO}_{2.25}$. However, for compositions above $\text{UO}_{2.25}$, the active oxide oxidized to a product which has less lattice distortion than the oxidation product of the inactive oxide. Electrical properties and lattice-parameter studies of the oxides in the composition range $\text{UO}_{2.25}$ to $\text{UO}_{2.4}$ indicate that the oxygen in excess of $\text{UO}_{2.25}$ is loosely bound in the cubic structure of the active oxide, but enters the lattice and takes definite positions in the tetragonal structure of the inactive oxide.

The electrical properties of oxides of composition U_4O_9 and U_3O_7 indicate that U_4O_9 does not exist at stoichiometric composition or in the excess-oxygen state. A distinct difference between UO_{2+x} and U_4O_{9-y} is evidenced by their electrical behavior, even though structurally these oxides are quite similar. Based upon conductivity and lattice-parameter measurements, the limit of the oxygen-to-uranium ratio in the UO_2 phase was established at 2.08 at 25 to 200 C, 2.11 at 400 C, 2.17 at 600 C, and 2.20 above 700 C. The composition limits of the U_4O_9 and U_3O_7 phases could not be established by the present work except to indicate very narrow single-phase regions.

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FIGURE 7. ISOTHERMAL CELL SIZE VERSUS OXYGEN CONTENT OF ACTIVE OXIDES UO_{2+x} AND U_4O_9

TABLE 4. UNIT-CELL DIMENSIONS OF THE ACTIVE UO_2 -OXYGEN SYSTEM

Temperature, C	Unit Cell Dimension, A								
	Two-Phase Samples(a)					Single-Phase Samples			
	$\text{UO}_{2.14}$	$\text{UO}_{2.16}$	$\text{UO}_{2.19}$	$\text{UO}_{2.21}$	$\text{UO}_{2.25}$	$\text{UO}_{2.30}$	$\text{UO}_{2.31}$	$\text{UO}_{2.38}$	$\text{UO}_{2.41}$
25	5.465	5.464	5.467	5.442	5.442	5.437	5.436	5.438	5.437
200		5.474	5.475	5.446	5.446	5.444			5.445
300		5.481	5.481	5.451					
400	5.483	5.485	5.482	5.458	5.458	5.456	5.458	5.457	5.456
500		5.488	5.486						
600	5.495	5.493	5.491	5.471	5.472	5.465	5.468	5.465	5.470
700		5.498			5.479				

(a) The lattice parameter of only the stronger phase was measured.

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