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THE UO_2 - UO_3 - Y_2O_3 SYSTEM AND EVALUATION OF THE $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ COMPOSITION

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**THE UO_2 - UO_3 - Y_2O_3 SYSTEM
AND EVALUATION OF THE
 $\text{UO}_{2.9}$ - $3\text{Y}_2\text{O}_3$ COMPOSITION**

**J.F. White
E.F. Juenke
D.E. Burgbacher**

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ABSTRACT

The tentative $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ ternary phase equilibrium diagram was developed for temperatures to 1700°C . Four phases were identified in the system at the temperatures between 1000°C and 1700°C : (1) U_3O_8 , (2) a face-centered cubic solid solution, (3) a body-centered cubic solid solution, and (4) a rhombohedral phase of the composition $(\text{U}, \text{Y})_7\text{O}_{12}$ ranging from 52.5 to 75 mole percent Y_2O_3 .

The rhombohedral phase ($\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$) was selected for detailed investigation as a nuclear fuel because it showed unusually good stability in air at elevated temperatures. Preparation, fabrication, and properties of this material are described including use of the material as a cladding on BeO tubes for high specific-power thermal-reactor fuel elements.

Property measurements of the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition show that it can be used in air for 500 hours at 1700°C without appreciable loss of UO_2 . The strength properties are about the same as those of UO_2 . Thermal expansion of the material is very similar to BeO which suggests its use on BeO as a fuel. Electrical conductivity of the material was found to be mainly electronic below 1500°C . Thermal conductivity is slightly lower than that of UO_2 .

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1. INTRODUCTION

This report covers the work performed under AEC Contract No. AT(40-1)-2847 on Job 57065, "UO₂.9·3Y₂O₃ Fuel Material," which terminated at the end of Fiscal Year 1963.

The objective of this task was to evaluate the UO₂-UO₃-Y₂O₃ ternary system for a fuel element material applicable to a high-temperature gas-cycle reactor system. This included a general study of the phase equilibria in the ternary system and a detailed investigation of the UO₂.9·3Y₂O₃ composition, the most refractory urania-bearing composition in the system.

The UO₂-UO₃-Y₂O₃ ternary system was studied to 1700°C with particular attention on the phases present at temperatures up to 1700°C. These studies resulted in two tentative phase equilibrium diagrams: one for temperatures up to 1000°C and another for temperatures from 1000° to 1700°C. The detailed investigation of the UO₂.9·3Y₂O₃ composition involved studies on fabrication, measurement of the physical and mechanical properties, and preliminary irradiation testing. This fuel composition was evaluated also as a cladding on BeO for use as a high specific power fuel element.

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2. UO_2 - UO_3 - Y_2O_3 SYSTEM

Previous investigations^{1,2,3*} of the UO_2 - UO_3 - Y_2O_3 system revealed the presence of four phases: (1) U_3O_8 , (2) a mixed oxide phase having the fluorite structure, (3) a phase having rhombohedral symmetry, and (4) a phase of the body-centered Y_2O_3 structure. In recent years, a number of studies⁴⁻¹¹ have been carried out on the solid solutions of the trivalent rare earth oxides La_2O_3 , Ce_2O_3 , Pr_2O_3 , Nd_2O_3 , and Sm_2O_3 with the tetravalent oxides ZrO_2 , CeO_2 , and PrO_2 . In each of the systems, a homogenous region having the fluorite structure was found to exist from 0 to about 45 mole percent R_2O_3 . Oxygen deficiency leads to random vacancies in the anion lattice as shown by X-ray line intensities and by correlation of density measurements with theoretical densities for anion vacancy and cation interstitial models.

In some of the systems, when the fluorite lattice becomes sufficiently anion deficient, the lattice transforms to rhombohedral symmetry. Baenziger et al.^{12,13} reported two different rhombohedral oxide structures for praseodymium ($\text{PrO}_{1.71}$ and $\text{PrO}_{1.85}$) and similarly for terbium oxide. The $\text{MO}_{1.71}$ rhombohedral structure also was identified in the UO_2 - UO_3 - Y_2O_3 system in air at the composition $\text{UO}_3 \cdot 3\text{Y}_2\text{O}_3$. Unpublished work by one of the authors of this report (Juenke) also established the existence of the rhombohedral phase solid solutions of uranium with oxides of La and the rare earths Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

Studies by Hund and Peetz⁵ and by Hund, Peetz, and Kottenbahn¹ showed that fluorite phases occur in solid solutions prepared at 1200°C in air by the reaction of U_3O_8 with various Group III oxides, including Y_2O_3 , La_2O_3 , and many of the other rare earth sesquioxides crystallizing with the "C-type" structure. For Y_2O_3 , the fluorite phase extended from 18 to 48 mole percent Y_2O_3 . Below 18 mole percent Y_2O_3 , a two-phase region was reported which consisted of U_3O_8 as one phase and the fluorite-boundary mixed crystal as the other. At about 38 mole percent Y_2O_3 , the cation and anion sites became fully occupied, and at higher concentrations of Y_2O_3 , anion vacancies were present. Near 48 mole percent Y_2O_3 , the authors reported the inability to attain complete conversion after heating at 1200°C for 8 hours in air.

Anderson, Ferguson, and Roberts,⁸ and Ferguson and Fogg⁹ reacted UO_2 and Y_2O_3 in vacuum at 2000°C to form fluorite solid solutions. X-ray and chemical analysis together with color changes indicated that these solid solutions had a strong affinity for oxygen, oxidizing rapidly in air at room temperature. Reacting UO_2 and Y_2O_3 in evacuated and sealed quartz capsules containing clean uranium metal at 1000°C for 1 to 3 days produced a highly reduced solid solution. Under these conditions, a fluorite solid solution was obtained from 0 to 48 mole percent Y_2O_3 . Between 48 and 64 mole percent Y_2O_3 , the measured fluorite cell constants behaved irregularly. Between 64 and 93 mole percent, a miscibility gap was observed. Beyond 93 mole percent, a body-centered cubic solid solution was observed.

Previous results on the behavior of mixed oxides prepared under both reducing and oxidizing conditions are somewhat incomplete in the Y_2O_3 -rich region. This report attempts

*Superscripts refer to the references listed in Section 5.

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to clarify some of the phase relationships in this region under various oxidizing and reducing conditions. A tentative phase diagram was constructed from the data obtained.

2.1 EXPERIMENTAL WORK

Urania-yttria solid solutions were prepared by blending Mallinckrodt grade UO_2 (purity 99.99 percent) and Y_2O_3 (purity 99.9 percent) powders. The homogenous mixture was fired in air in platinum or zirconia crucibles at 1480°C for 60 hours. The powders were then reduced in a hydrogen atmosphere at various temperatures and times. Some compositions were reacted directly in hydrogen without pre-reacting in air and showed no difference in the X-ray diffraction pattern. The X-ray and chemical analyses were performed after each treatment and are summarized in Table 2.1. One composition (60 mole percent Y_2O_3) was pre-reacted at 1850°C in air for 2 hours before reduction in hydrogen to overcome the apparently slow reaction rate characteristic of this composition. Compositions which were urania-rich showed a tendency to oxidize spontaneously in air at room temperature and were handled under an argon blanket to prevent oxidation.

The hydrogen-reduced compositions were re-oxidized in air at low temperatures ($< 540^\circ\text{C}$) and at high temperatures ($> 1300^\circ\text{C}$). These results are summarized in Table 2.1. The amounts of each phase present were determined quantitatively by comparing the relative contribution of the most prominent X-ray peak intensities for each phase. The phase boundaries in two-phase regions were then determined by application of the "lever" rule. The oxygen-to-uranium ratio was determined by chemical analysis for U^{+4} and total uranium, and the U^{+6} content was determined by difference. An intermediate level in the oxidation state was obtained by heating powders in a 10:1 CO_2 -CO atmosphere. As shown in Table 2.2, both oxidized and reduced solid solutions were used as starting materials to determine if equilibrium could be established. A heat treatment of 20 hours at 1500°C was considered sufficient to reach equilibrium; however, the rate of approach to equilibrium from the oxidized direction appeared to be slower, particularly at the 60 mole percent Y_2O_3 composition.

For reacted compositions heated in hydrogen at 1700°C , the structures were believed to be essentially at equilibrium, although this was not determined in all cases. The degree of reduction increased with higher heating temperatures or lower oxygen partial pressures. During oxidation below 500°C , the oxygen-to-uranium ratio comes to equilibrium in a few hours with respect to whatever lattice structure is present as a result of reduction at high temperatures; during oxidation at high temperatures, it equilibrated rapidly relative to the sluggish structure changes which require cation mobility as well as anion mobility.

2.2 PHASE DIAGRAM

The ternary phase diagram is shown for two temperature regions, between 1000° and 1700°C and below 1000°C . The higher temperature diagram shown in Figure 2.1 represents essentially an equilibrium system where the solid lines represent established phase boundaries and the dashed lines represent probable boundaries which are not well established. The lighter dashed lines describe the approximate composition line for three conditions: (1) hydrogen, -40°C dewpoint, 1700°C ; (2) air, 1000°C ; and (3) $10\text{CO}_2 - 1\text{Co}$ at 1500°C . The symbols designate the phases observed at the various compositions. Two-phase regions are indicated by overlapping symbols.

The region along the UO_2 - UO_3 join was not studied in this work; this portion of the diagram was constructed from the work of others.¹⁴ The extent of the solubility of Y_2O_3 in the U_4O_9 phase or in the U_3O_8 phase was not determined. The UO_3 corner was not constructed because its stable range occurs at pressures which are outside the range of interest. The region along the UO_2 - Y_2O_3 join was drawn from the results of the work done

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TABLE 2.1
PHASE RELATIONSHIPS AND OXYGEN-TO-URANIUM RATIOS
IN THE UO_2 - UO_3 - Y_2O_3 SYSTEM AFTER VARIOUS HEAT TREATMENTS

Composition		Hydrogen Reaction ^a				Low-Temperature Oxidation				High-Temperature Oxidation				Air Reaction			
UO_2 Mole %	Y_2O_3 Mole %	Temperature, °C	Time, hr	Phases	O/U ^b	Temperature, °C	Time, hr	Phases	O/U ^b	Temperature, °C	Time, hr	Phases	O/U ^b	Temperature, °C	Time, hr	Phases	O/U ^b
12.5	87.5	1650 ^c	3	BCC	2.03	540	2	BCC	2.8	1315	45	50% BCC - 50% Rh I					
		1700	12	BCC	2.28	540	65	BCC		1400	16	55% BCC - 45% Rh I	2.99				
		1700 ^d	18	93% BCC - 7% Rh I	2.24					1400	16	45% BCC - 55% Rh I	2.99				
14.3	85.7	1700 ^d	18	90% BCC - 10% Rh I	2.23												
16.7	83.3	1650 ^c	3	BCC - Trace FCC	2.04	540	2	BCC - Trace FCC		1400	16	30% BCC - 70% Rh I	2.99				
		1700 ^d	18	88% BCC - 12% Rh I	2.25					1400	16	22% BCC - 78% Rh I	2.99				
20.0	80.0	1700 ^d	18	83% BCC - 17% Rh I	2.27												
22.2	77.8	1700	12	72% BCC - 28% Rh I	2.25	288	71	72% BCC - 28% Rh II									
25.0	75.0	1650 ^c	3	70% BCC - 30% FCC	2.10	540	2	70% BCC - 30% FCC	2.8	1400	16	10% BCC - 90% Rh I	2.97	1650	2	100% Rh I	
		1700 ^d	18	70% BCC - 30% Rh I	2.20					1315	5	100% Rh I		1370	16	100% Rh I	2.99
		1700	30	72% BCC - 28% Rh I	2.28	540	20	72% BCC - 28% Rh II									
30.8	69.2	1650 ^c	3	60% BCC - 40% FCC	2.06	540	2	60% BCC - 40% FCC	2.9	1480	100	60% Rh I - 40% FCC		1370	25	80% Rh I - 20% FCC	
		1700	66	60% BCC - 40% Rh I	2.27	288	71	60% BCC - 40% Rh II	2.71								
33.3	66.7	1700	66	44% BCC - 56% Rh I	2.28	288	71	44% BCC - 56% Rh II	2.79	1650	16	50% Rh I - 50% FCC		1370	25	80% Rh I - 40% FCC	
40.0	60.0	1540	3	Rh I	2.3	260	52	Rh II		1315	4	Trace Rh I - FCC		1850	2	100% FCC	
		1700	12	20% BCC - 80% Rh I	2.2	540	25	20% BCC - 80% Rh II		1850	5	100% FCC					
										1460	16	Trace Rh I - FCC					
45.5	54.5	1700	12	15% BCC - 85% Rh I	2.25	288	71	15% BCC - 85% Rh II									
50.0	50.0	1700	66	30% Rh I - 70% FCC	2.58 ^e	288	71	30% Rh II - 70% FCC	2.88					1370	25	100% FCC	2.88
60.0	40.0	1700	66	100% FCC	2.63 ^e	288	71	100% FCC	2.67					1370	25	100% FCC	2.68
66.7	33.3	1700	12	100% FCC	- ^e	288	65	100% FCC	2.52					1300	16	100% FCC	2.52
71.5	28.5	1700	12	100% FCC	- ^e	288	65	100% FCC	2.44					1300	16	90% FCC - 10% U_3O_8	2.53
77.7	22.3	1700	12	100% FCC	- ^e	288	65	100% FCC	2.36					1300	16	70% FCC - 30% U_3O_8	2.56
82.5	17.5	1700	12	100% FCC	- ^e	288	65	100% FCC	2.26					1300	16	50% FCC - 50% U_3O_8	2.59
88.3	11.7	1700	12	100% FCC	- ^e	288	65	100% FCC	2.18					1300	16	36% FCC - 64% U_3O_8	2.62
95	5	1700	40	FCC + Trace UO_{2+x}	2.05	288	24	FCC FCC Trace Tetrag. U_3O_7		800°C	24	U_3O_8 Trace FCC					
98	2	1700	60	70% FCC + 30% UO_{2+x}	2.04	288	24	70% FCC + 30% Tetrag. U_3O_7		800°C	24	U_3O_8 Trace FCC					

^aReacted in H_2 , dewpoint -40°C unless otherwise noted.

^bOxygen-to-uranium ratios recorded as two significant figures are estimated values, three significant figures are chemical analysis results.

^cReduced for 1 hour at 2000°C then heated at 1650°C in H_2 .

^dReacted in H_2 , dewpoint 0°C.

^eSpontaneously oxidized upon exposure to air.

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TABLE 2.2
PHASE RELATIONSHIPS AND OXYGEN-TO-URANIUM RATIOS IN THE $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ SYSTEM
AFTER VARIOUS HEAT TREATMENTS IN A $10\text{CO}_2 - 1\text{CO}$ ATMOSPHERE AT 1500°C

Composition State Of Materials ^a	49 $\text{UO}_2\text{:1Y}_2\text{O}_3$		19 $\text{UO}_2\text{:1Y}_2\text{O}_3$		7.5 $\text{UO}_2\text{:1Y}_2\text{O}_3$		2.5 $\text{UO}_2\text{:1Y}_2\text{O}_3$		2 $\text{UO}_2\text{:1Y}_2\text{O}_3$	
	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized
O/U Ratio and Phases - Starting Materials ^b	2.04 - 70% FCC 30% UO_{2+x}	-	2.05 - FCC Trace UO_{2+x}	-	- FCC ^d	-	- FCC ^d	-	- FCC ^d	-
O/U Ratio and Phases After Time at 1500°C (5 hr)	-	-	-	-	-	-	-	-	-	-
(10 hr)	-	-	-	-	-	-	-	-	-	-
(24 hr)	2.04 - FCC Trace UO_{2+x}	-	2.06 - FCC Trace UO_{2+x}	-	2.22 - FCC	-	2.38 - FCC	-	2.44 - FCC	-
<hr/>										
Composition State Of Materials ^a	3 $\text{UO}_2\text{:2Y}_2\text{O}_3$		1 $\text{UO}_2\text{:1Y}_2\text{O}_3$		2 $\text{UO}_2\text{:3Y}_2\text{O}_3$		1 $\text{UO}_2\text{:2Y}_2\text{O}_3$		4 $\text{UO}_2\text{:9Y}_2\text{O}_3$	
	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized
O/U and Phases - Starting Materials ^b	2.1 - FCC ^d	-	2.1 - 25% Rh I 75% FCC	2.88 - 15% Rh I 85% FCC	2.2 - 80% Rh I 20% BCC	3.0 - FCC	2.28 - 15% Rh I 85% BCC	3.0 - 60% Rh I 40% FCC	2.27 - 40% Rh I 60% BCC	3.0 - 80% Rh I 20% FCC
O/U and Phase after Time at 1500°C (5 hr)	-	-	2.59 - FCC ^d	-	2.63 - 60% Rh I 40% FCC	-	2.64 - 65% Rh I 35% FCC	2.86 - 40% Rh I 20% BCC	- { 95% Rh I 5% BCC	- { 80% Rh I 20% FCC
(10 hr)	-	-	-	-	-	-	-	-	2.64 - 95% Rh I 5% BCC	2.84 - Rh I Trace FCC
(24 hr)	2.58 - FCC	-	2.58 - 35% Rh I ^e 65% FCC	2.67 - 20% Rh I ^e 80% FCC	2.67 - 60% Rh I 40% FCC	2.85 - 30% Rh I 70% FCC	2.63 - 95% Rh I 5% FCC	2.68 - 85% Rh I 15% FCC	2.65 - 90% Rh I 10% BCC	2.66 - 95% Rh I 5% BCC
<hr/>										
Composition State Of Materials ^c	1 $\text{UO}_2\text{:3Y}_2\text{O}_3$		1 $\text{UO}_2\text{:4Y}_2\text{O}_3$		1 $\text{UO}_2\text{:5Y}_2\text{O}_3$		1 $\text{UO}_2\text{:6Y}_2\text{O}_3$		1 $\text{UO}_2\text{:7Y}_2\text{O}_3$	
	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized
O/U and Phases - Starting Materials ^b	2.20 - 28% Rh I 72% BCC	2.98 - Rh I	2.27 - 17% Rh I 83% BCC	-	2.25 - 12% Rh I 88% BCC	-	2.23 - 10% Rh I 90% BCC	-	2.24 - 7% Rh I 93% BCC	-
O/U and Phase after Time at 1500°C (5 hr)	2.61 - Rh I BCC	-	-	-	-	-	-	-	-	-
(10 hr)	-	-	-	-	-	-	-	-	-	-
(24 hr)	2.66 - 72% Rh I 28% BCC	2.73 - 80% Rh I 20% BCC	2.61 - 45% Rh I 55% BCC	-	2.65 - 40% Rh I 60% BCC	-	2.58 - 30% Rh I 70% BCC	-	2.64 - 25% Rh I 75% BCC	-

^aReduced: Reacted 12 to 70 hours at 1700°C in H_2 . Oxidized: Reacted 12 to 24 hours at 1300° to 1400°C in Air.

^bO/U ratio recorded as two significant figures are estimated values, three significant figures are chemical analysis results.

^cReduced: Reacted 18 hours at 1700°C in H_2 (dewpoint, 0°C).

^dSpontaneous oxidation in laboratory air observed.

^eHeated 50 hours.

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Fig. 2.1 - The $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ ternary diagram from 1000° to 1700°C

in vacuum at 2000°C by Anderson, et al.⁸ The Y_2O_3 corner is somewhat complex and is not completely understood. It appears that urania solubility in the body-centered cubic (BCC) phase decreases from about 14 mole percent UO_2 to approximately 0 mole percent UO_3 .

The low-temperature diagram, Figure 2.2, shows the phases present before and after oxidation at the indicated temperature. Some of these structures are metastable and transform to the equilibrium structure when heated above 1000°C . In this temperature region, a second rhombohedral phase (Rh II) was observed between 50 and 60 mole percent Y_2O_3 in air. This phase transformed to a face-centered cubic (FCC) phase at temperatures above 1000°C . The crystalline phases present in the system are discussed below.

Face-Centered Cubic Fluorite Phase

Solid solutions of UO_{2+x} with Y_2O_3 that have a FCC structure are well established. The primary interest in this work was determining the single-phase region and changes in unit cell size with composition and oxidation state. The fluorite structure extends from about 0 to 45 mole percent Y_2O_3 under strongly reducing conditions. These materials oxidize rapidly in air at room temperature, and oxygen readily diffuses into vacant anion sites. This results in a shrinkage of the unit cell which was observed by X-ray diffractometry

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Fig. 2.2 – The $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ system (low-temperature oxidation below 1000°C)

(see Figure 2.3). The composition $1\text{UO}_2 \cdot 1\text{Y}_2\text{O}_3$ is the most sensitive since it contains the largest number of vacancies. Chemical analysis indicates an oxygen-to-uranium ratio of about 2.67 after spontaneous oxidation of this composition.

As the oxygen-to-uranium ratio is increased, the fluorite-phase region becomes narrower. The fluorite boundary on the oxygen-deficient side occurs in the vicinity of 50 mole percent Y_2O_3 and may be variable depending on the temperature. At 50 mole percent Y_2O_3 , both a single-phase FCC and two-phase FCC and Rh I mixture were obtained, hence the exact location of the boundary is not known.

There is no indication, within the accuracy of measurement, that excess oxygen atoms occupy interstitial positions in the lattice at high temperatures ($> 1000^\circ\text{C}$) in air when the yttria content is above 20 mole percent. Results of thermodynamic measurements by Aronson and Belle¹⁵ indicate that an oxygen-excess solid solution of $\text{MO}_{2.03}$ composition could be made at 15 mole percent Y_2O_3 . At low temperatures, the amount of interstitial oxygen appears to be increasing as the yttria content is decreased and approaches the limiting value near $\text{MO}_{2.25}$ at 0 percent Y_2O_3 . As the Y_2O_3 concentration is decreased, the lattice expansion probably permits increasing amounts of interstitial oxygen.

At low yttria concentrations (2 to 5 mole % Y_2O_3), both UO_{2+x} and $(\text{U}, \text{Y})\text{O}_{2.0}$ phases were present after heating repeatedly in $\text{CO}_2\text{-CO}$ or in hydrogen atmospheres. In lieu of dissolving

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Fig. 2.3.—Comparison of equivalent cubic lattice parameter of $(U_{1-x}Y_x)O_{2.25-y}$ composition as a function of cation fraction of yttrium

interstitial oxygen, the urania-yttria solid solution may reject a small amount of UO_{2+x} so that the solid solution remains at the stoichiometric composition, MO_2 . One experiment carried out in Ar - 1 volume percent O_2 at $1500^\circ C$ to determine if three phases, UO_{2+x} , $(U, Y)O_2$, and U_3O_8 , could be formed resulted in only a U_3O_8 and a $(U, Y)O_2$ phase. The fluorite boundary on the oxygen-excess side near the UO_2 corner is tentatively drawn as a curved line which departs from the stoichiometric $(U, Y)O_2$ line and intersects the UO_2 - UO_3 boundary at $UO_{2.25}$.

The change in lattice parameter for the fluorite cell as a function of yttrium atom fraction is shown in Figure 2.3. The data of Ferguson and Fogg⁹ are included to indicate the variation in lattice parameter at a constant oxygen-to-uranium ratio of about 2.0. The fluorite lattice parameters after high-temperature treatment in CO_2 - CO atmosphere represent a composition of constant oxygen-to-metal ratio ($y = 0.25$). The lattice parameters after low-temperature oxidation are also for compositions at oxygen-to-metal ratios of 2.0 at high yttria content, but as the yttria content is decreased the compositions absorb excess oxygen and the lattice parameter approaches the lattice constant for $UO_{2.25}$.

Rhombohedral Phases (Rh I and Rh II)

The existence of a rhombohedral phase at an oxygen-to-metal atom ratio of 12:7 was reported previously.³ This structure (Rh I) can occur over the composition range from about

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$17\text{UO}_2 \cdot 17 \cdot 18\text{Y}_2\text{O}_3$ to $1\text{UO}_3 \cdot 0 \cdot 3\text{Y}_2\text{O}_3$. At low-oxidation levels, there is probably a random distribution of metal ions in the oxygen matrix, while in the fully oxidized state a highly ordered arrangement is indicated.

A closely related rhombohedral phase (Rh II) was found to exist at a constant oxygen-to-metal atom ratio of 15:8, with a composition range from $17\text{UO}_2 \cdot 67 \cdot 18\text{Y}_2\text{O}_3$ to $2\text{UO}_3 \cdot 3\text{Y}_2\text{O}_3$. This is probably a metastable phase since it was observed only as a low-temperature intermediate compound during the oxidation of Rh I. This transformation from the Rh I to Rh II structure can be explained by a partial filling of oxygen sites. This mechanism is evidenced in the change in X-ray diffraction patterns; the extra lines attributed to the rhombohedral structure decrease markedly in intensity after oxidation.

Hexagonal unit cell dimensions and volume of the rhombohedral phases are compared in Table 2.3. Decreasing cell size is caused by both a compositional change as well as the substitution of U^{+6} for U^{+4} ions.

TABLE 2.3
HEXAGONAL UNIT CELL DIMENSIONS FOR
THE RHOMBOHEDRAL PHASES

Rh I Composition (Oxygen-To-Metal = 1.714)	Lattice Constants, Å	Rh II Composition (Oxygen-To-Metal = 1.875)	Lattice Constants, Å
$17\text{UO}_2 \cdot 17 \cdot 18\text{Y}_2\text{O}_3$	a = 10.002 c = 9.362 Volume = 817.09	$17\text{UO}_2 \cdot 67 \cdot 18\text{Y}_2\text{O}_3$	Not measured
$2\text{UO}_2 \cdot 36 \cdot 3\text{Y}_2\text{O}_3$	a = 10.002 c = 9.353 Volume = 811.31	$2\text{UO}_3 \cdot 0 \cdot 3\text{Y}_2\text{O}_3$	a = 9.943 c = 9.289 Volume = 796.14
$4\text{UO}_2 \cdot 67 \cdot 9\text{Y}_2\text{O}_3$	a = 9.967 c = 9.338 Volume = 804.25		
$1\text{UO}_3 \cdot 0 \cdot 3\text{Y}_2\text{O}_3$	a = 9.934 c = 9.364 Volume = 801.13		

The pseudo-fluorite lattice parameter for the rhombohedral phase (Rh I) is compared in Figure 2.3 with the lattice parameters for the FCC phase. It can be noted that under oxidizing conditions, the limiting fluorite phase at $\text{UO}_3 \cdot 1.5\text{Y}_2\text{O}_3$ (60 mole % Y_2O_3) and the Rh I phase $\text{UO}_3 \cdot 3\text{Y}_2\text{O}_3$ (75 mole % Y_2O_3) have very little difference in cell volume.

Body-Centered Cubic Phase

Yttria crystallizes in a BCC structure (rare earth C-type). The solubility of urania at high temperatures in this phase extends from about 14 mole percent UO_2 ($1\text{UO}_2 \cdot 6\text{Y}_2\text{O}_3$) to 0 mole percent UO_3 . Low-temperature oxidation increases the solubility limit somewhat as indicated in Figure 2.4. From these data, it appears that the unit cell containing 16 molecules Y_2O_3 cannot accept more than about two additional oxygen atoms into its structure. This means that the maximum oxygen-to-metal ratio for BCC solid solutions is about 1.56 at temperatures below 1000°C.

The BCC solid solution is not stable in air at temperatures above 1000°C; therefore, the preparation of a homogeneous solid solution requires reaction in hydrogen at high temperatures. The 87.5 mole percent Y_2O_3 composition was prepared in the oxidized state by low-temperature oxidation after reaction in hydrogen at 1700°C. Oxidation of the BCC powder

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Fig. 2.4 — Lattice parameters of BCC solid solution of UO₂-Y₂O₃

(average surface area of 0.08 m²/g) readily occurred at temperatures above 400°C. The behavior of the BCC solid solution is shown in Table 2.4 after various heat treatments. Oxidation at temperatures below 815°C resulted in an increase in the oxygen-to-uranium ratio of 0.67. After further oxidation at temperatures above 1100°C, this increase in the oxygen-to-uranium ratio was 0.85 as a result of the decomposition of the BCC solid solution to essentially free Y₂O₃ and Rh I phase. The Rh I phase (75 mole percent Y₂O₃), which contains nearly all of the uranium, has an oxygen-to-uranium ratio of about 3.0 at temperatures below 1300°C. By difference, the initial oxygen-to-uranium ratio must be about 2.15 which is consistent with the oxygen-to-uranium ratios determined by chemical analysis for

TABLE 2.4
BEHAVIOR OF COPRECIPITATED UO_{2+x}·7Y₂O₃ (87.5 mole % Y₂O₃) SOLID SOLUTION
AFTER VARIOUS HEAT TREATMENTS

Experiment	Original Material	Atmosphere	Temperature, °C	Time, min	Change In Oxygen-To-Uranium Ratio	X-Ray Diffraction Analysis
1	Coprecipitated ^a	Air	815	960	-	BCC SS
2	Material from experiment 1	Air	1400	3600	-	50% Rh I 50% Free Y ₂ O ₃
3	Coprecipitated	H ₂	1700	720	-	BCC SS
4	Material from experiment 3	O ₂ (140 mm)	650	1750	0.67	BCC SS
5	Material ^b from experiment 3	O ₂ (130 mm)	816	910	0.67	Not determined
6	- ^b	O ₂ (130 mm)	1315	2710	0.85	Not determined
7	- ^b	O ₂ (130 mm)	816	300	0.85	50% Rh I 50% Free Y ₂ O ₃

^aThe starting material was coprecipitated as 1UO_{2+x}·7Y₂O₃ by adding NH₄OH solution to a stirred aqueous solution of uranyl and yttrium nitrates. The product is probably a mixed crystal of diammonium uranate and yttrium hydroxide. Calcination was essentially complete in air at 800°C in a few hours.

^bExperiments 5, 6, and 7 were performed sequentially on the same material.

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BCC solid solutions reduced at 1700°C. The maximum oxidation state of the uranium in the BCC phase at temperatures below the decomposition temperature must then be about 2.8.

A plot of the change in lattice parameter of the pseudo-fluorite cell (one-half the lattice parameter of the BCC unit cell) with urania content is given in Figure 2.4. The contraction which accompanies oxidation of these solid solutions was very small.

The FCC and BCC solid solutions coexist over a small region of the phase diagram at low oxygen-to-uranium ratios (<2.1). Samples containing both phases will oxidize at temperatures below 1000°C without a phase change; in fact, oxidation at low temperatures produces no crystal transformation over the whole composition region studied. Temperatures above 1000°C are required to give the cations enough mobility to rearrange into a different structure.

System Above 1700°C

Studies of the phase relationships in the $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ system at temperatures in the range of 1700° to 2000°C were limited to the determination of the phase relationships at the $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ composition.

Pressed $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ pellets were heated for 2 to 4 hours in a closed crucible of the same composition. The furnace atmosphere consisted of about 90-percent argon and about 10-percent air. The phases present and the oxygen-to-uranium ratios were determined by X-ray diffraction and chemical analysis. Table 2.5 summarizes the experimental data and includes data for the same composition heated in flowing oxygen (oxygen-to-uranium ratio 2.7 to 2.8) at comparable temperatures.

TABLE 2.5
PHASES PRESENT AS A FUNCTION OF OXYGEN-TO-URANIUM RATIO
FOR THE $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ COMPOSITION AFTER
HEATING AT HIGH TEMPERATURES

Temperature, °C	Atmosphere	Oxygen-To-Uranium Ratio	Phases Present
1800	Oxygen	2.78	Rh I + BCC
	Argon - Air	2.25	60% BCC + 40% FCC
1900	Oxygen	2.78	Rh I + BCC
	Argon - Air	2.27	Major BCC - Minor FCC
2000	Argon - Air	2.24	Major BCC - Minor FCC
	Oxygen	2.73	Major Rh I - Minor BCC
	Oxygen	2.76	Major Rh I - Minor BCC
	Argon - Air	2.07	Major BCC + Minor FCC

The results indicate that at temperatures above 1700°C a broadening of the FCC and BCC region to higher oxygen-to-uranium ratios occurs in the vicinity of the $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ composition. At temperatures of 1700°C and below, the two-phase BCC and FCC region extends only to oxygen-to-uranium ratios of about 2.10.

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3. $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ COMPOSITION

3.1 FABRICATION

Preparation of Powder

Early work¹⁶ on the mechanism and kinetics of forming $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ showed that, if the material had full access to air, the reaction between UO_2 and Y_2O_3 is complete in 24 hours at 1360°C . Subsequent studies on this reaction resulted in a process whereby the UO_2 and Y_2O_3 were mixed by milling for 30 minutes in a vibratory mill and then reacted for 8 hours at 1375°C in air. After reaction at this temperature, the material had an oxygen-to-uranium ratio of 2.98 to 3.0. The reacted material was milled for 4 hours in a vibratory mill to produce a sinterable powder with a surface area of 0.025 square meters per gram (measured by the BET method using krypton gas). This reacted and milled $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ powder is then suitable for subsequent processing into test bodies by pressing or by extrusion.

Vibratory milling was selected for processing reacted $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ because earlier work¹⁷ showed that this method was more efficient than rotary milling. The powder, grinding media, and vehicle were put into the mill chamber, a rubber-lined steel container. This container was vibrated by a conventional 3.8-liter (1-gallon)-capacity paint conditioner, which has a three-dimensional, high-frequency (650 cycles per minute), high-amplitude vibration.

The grinding media used was sintered Y_2O_3 pellets about 0.32 centimeter (1/8 inch) in diameter and about 0.32 centimeter (1/8 inch) in length; the vehicle used was water. The mill was loaded to about 65 percent capacity.

The comminution variables studied were (1) the volume ratio of $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ to grinding media, (2) the volume ratio of water to $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$, and (3) the milling time. The sinterability of the milled powder was determined by pressing 0.95-centimeter (3/8-inch)-diameter, 1.27-centimeter (1/2-inch)-long pellets at 281 kg/cm^2 (4000 psi) in a steel die, by isostatically compacting at 1406 kg/cm^2 (20,000 psi), and by sintering for 4 hours at 1730° to 1750°C in oxygen. The Y_2O_3 increase from the grinding media was determined by wet chemistry.

Figure 3.1 shows the effect of varying the grinding media-to- $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ ratio on sintered density and Y_2O_3 increase. The results show that a volume ratio of about 3.6:1 (grinding media-to- $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$) is sufficient for the desired density.

The effect of the $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ -to-water ratio on sintered density is given in Figure 3.2. These data indicate that a ratio of water to $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ of between 2:1 and 3:1 by volume is suitable to produce sinterable powder. However, a ratio greater than 2.5:1 causes a rapid increase in Y_2O_3 contamination.

Figure 3.3 shows the effect of milling time on sinterability. Milling times of between 2 and 4 hours are sufficient to produce sinterable powders, and the material has less than 1.5 percent Y_2O_3 contamination.

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Fig. 3.1 - Effect of grinding media-to-powder ratio on sintered density and Y_2O_3 pickup

Fig. 3.2 - Effect of water-to-powder ratio on sintered density and Y_2O_3 pickup

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Fig. 3.3—Effect of milling time on sintered density and Y₂O₃ pickup

Based on these results, the milling process selected was a volume ratio of 1UO₂.9·3Y₂O₃ to 3.6 media to 2.5 water, with a 4-hour milling time. The Y₂O₃ contamination of about 1.2 weight percent (based on the Y₂O₃ content of the UO₂.9·3Y₂O₃ powder) is compensated by adjusting the starting UO₂.9·3Y₂O₃ composition.

Cold Pressing

Pieces such as pellets, thermal conductivity specimens, and other bodies of similar shape may be formed by dry pressing in a steel die at 352 kg/cm² (5000 psi) followed by isostatic pressing at 1406 kg/cm² (20,000 psi). Use of about 2 weight percent Mobilcer "R" Wax as a binder facilitated handling.

Extrusion and Coextrusion

A plastic dispersion mass of the UO₂.9·3Y₂O₃ composition was developed for use in co-extruding this material as the inside diameter cladding on BeO tubes. The best plasticizer developed was an aqueous solution of mixed polymers modified with glycerine. The polymers used were hydroxymethyl cellulose (a strongly cross-linked polymer) and polyacrylamide (a linear chain polymer).

The pressure - flow relationships of four different UO₂.9·3Y₂O₃ plastic dispersion masses are shown in Figures 3.4, 3.5, 3.6, and 3.7 to illustrate development of a plastic dispersion mass of this material. Figure 3.4 shows the flow properties using polyacrylamide as a plasticizer. The erratic behavior shown in the flow causes a "chattering" of the material during coextrusion with BeO, and results in non-uniformity of cladding thickness. Using glycerine to replace part of the polyacrylamide and part of the water results in a smooth pressure versus flow curve (Figure 3.5), but this plasticizer requires a high pressure change to give relatively low changes in flow rate. This causes excessive pressure to develop during coextrusion.

The other extreme of very rapid changes in flow with small changes in pressure occurs with hydroxymethyl cellulose, as shown in Figure 3.6 (only shown as modified with glycerine). By combining these two systems, a more desirable flow curve is obtained, as shown in Figure 3.7.

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Fig. 3.4 – Extrusion pressure versus extrusion flow rate of $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ dispersed in a solution of 20 percent polyacrylamide in H_2O

Fig. 3.5 – Extrusion pressure versus extrusion flow rate of $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ dispersed in a solution of 15 percent polyacrylamide, 20 percent glycerine, and 65 percent H_2O

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Fig. 3.6—Extrusion pressure versus extrusion flow rate of $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ dispersed in a solution of 15 percent hydroxy-methyl cellulose, 20 percent glycerine, and 65 percent H_2O

Fig. 3.7—Extrusion pressure versus extrusion flow rate of $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ dispersed in a solution of 4 percent polyacrylamide, 10 percent hydroxy-methyl cellulose, 6.7 percent glycerine, and 79.3 percent H_2O

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These effects can be expressed in terms of the differences between pressures required to give flow rates of 0.25 centimeter (0.1 inch) per second and 1.25 centimeter (0.5 inch) per second for each material. The pressure differences are 65, 1.1, and 22.5 kg/cm² (930, 15, and 320 psi), respectively, for the polyacrylamide, hydroxymethyl cellulose, and the mixture of the two polymers.

Dip Coating

A procedure was developed for applying a BeO cladding to the inside diameter of co-extruded BeO-UO_{2.9}·3Y₂O₃ tubes so that fission product release is inhibited during irradiation tests. This process was a dip-coating technique using approximately 1 weight percent ammonium alginate in water to give a suspension of the BeO. Vibratory milling of the BeO increased the density of the cladding and produced a smoother, more uniform coating. As shown in Figure 3.8, the cladding is continuous and dense (estimated 2 to 4 percent porosity). Cladding thickness measured at sections cut from opposite ends of a tube was 0.058 ± 0.0025 millimeter (0.0023 ± 0.0001 inch).

Fig. 3.8—Coextruded BeO-UO_{2.9}·3Y₂O₃ tube dip coated with BeO cladding and sintered for 2 hours at 1650°C in air

Sintering

The milled UO_{2.9}·3Y₂O₃ powder sinters to about 99.7 percent of theoretical density after 3 hours at 1750°C in an oxygen atmosphere. The oxygen-sintered material shows about 5 percent or less body-centered cubic (BCC) phase to be present. The grain size of the material is about 6 microns. A photomicrograph of a typical structure is shown in Figure 3.9.

Sintering in a hydrogen atmosphere for about 12 hours at 1700°C produces a structure composed of the rhombohedral reduced phase plus a body-centered cubic phase. The density is about 99.1 percent of theoretical with an oxygen-to-uranium ratio of about 2.20. The grain size is about 3 microns. Subsequent oxidation of the sintered part changes the oxygen-

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to-uranium ratio to 2.9 to 3.0 depending on the temperature at which the oxidation is equilibrated. A typical microstructure of hydrogen-sintered $\text{UO}_{2.2} \cdot 3\text{Y}_2\text{O}_3$ is shown in Figure 3.10. The structure after subsequent oxidation at 1450°C is shown in Figure 3.11.

3.2 CHEMICAL AND PHYSICAL PROPERTIES

Fuel Retention and Phase Stability

Microstructural studies, X-ray diffraction, and chemical analyses were used to evaluate the high-temperature stability of the rhombohedral $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ composition. Specimens, both sintered pellets and powders, were heated for extended times in oxidizing atmospheres at temperatures of 1650° to 2000°C . The UO_2 loss and structure change data for sintered pellet specimens are summarized in Table 3.1 for various times in oxidizing atmospheres (air or oxygen) at 1700° to 2000°C .

TABLE 3.1
COMPOSITION AND PHASES PRESENT FOR $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ PELLETS AFTER
HIGH-TEMPERATURE TESTS IN OXIDIZING ATMOSPHERES

Temperature, $^\circ\text{C}$	Time, hr	Oxygen-To- Uranium Ratio	$\text{UO}_{2.9}$ Loss, %	Phases Present	
				Exterior	Interior
As-sintered	-	2.92	-	Rhombohedral (Rh I) Trace body-centered cubic (BCC)	Rh I, Trace BCC
1700 (air)	100	2.91	nil	Rh I, Trace BCC	
	500	2.92	nil	Major BCC Minor Rh I	Major Rh I Trace BCC
	1005	2.90	2.9	Major BCC Trace unidentified	Major Rh I Trace BCC
1850 (O_2)	19	2.85	6.0	Rh I, BCC, Trace unidentified	Rh I, Trace BCC
	23	-	-	Rh I, BCC, Possible face-centered cubic (FCC)	Rh I, BCC
1900 (O_2)	11	2.79	6.6	Major Rh I Minor BCC	Major Rh I Minor BCC
	17	2.79	2.9	Major Rh I Minor BCC	Major Rh I Minor BCC
2000 (O_2)	1	2.80	1.3	50% BCC - 50% Rh I	Rh I
	5	2.80	1.3	BCC - Rh I	Rh I

The samples which were tested at 1800°C and higher picked up a small amount (1 to 2 wt %) of ZrO_2 from the furnace fixtures. The effect, if any, of this contamination was not determined.

The data, summarized in Table 3.1, show the following:

1. After 500 hours at 1700°C , no loss of UO_2 was detected by chemical analysis. However, X-ray diffraction analysis of polished sections showed the presence of a second phase determined to be body-centered cubic (BCC) solid solution. The oxygen-to-uranium ratio of 2.92 for the specimen and the identification of the second phase are in agreement with the phase diagram shown in Figure 2.1. After 1000 hours at 1700°C , the surface of the specimen was depleted of UO_2 , resulting in a single, Y_2O_3 -rich BCC phase.

Neg. 555

500 X

Fig. 3.9—Microstructure of milled $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ powder sintered in oxygen for 3 hours at 1750°C

Etched in warm H_2SO_4 solution
Density — 99.7% of theoretical
Grain size — 6 microns

Neg. 461

500 X

Fig. 3.10—Microstructure of $\text{UO}_{2.2}\cdot 3\text{Y}_2\text{O}_3$ sintered in hydrogen for 12 hours at 1700°C

Etched in warm H_2SO_4 solution
Density — 99.1% of theoretical
Grain size — <3 microns

Neg. 462

500 X

Fig. 3.11—Microstructure of $\text{UO}_{2.2}\cdot 3\text{Y}_2\text{O}_3$ sintered in hydrogen for 12 hours at 1700°C and then normalized in air for 60 hours at 1450°C

Etched in warm H_2SO_4 solution
Density — 99.4% of theoretical
Grain size — 3 microns

2. In a short time (19 hours) at 1850°C and above, a breakdown of the rhombohedral (Rh I) phase occurs; X-ray and microscopic examination showed two or more phases to be present. Figure 3.12 shows the microstructure of an as-sintered specimen. The formation of the second phase at 1850°C is shown in Figure 3.13. Figure 3.14 shows a sample after 11 hours at 1900°C treatment. As expected, the BCC phase concentration at 1900°C was greater than that at 1850°C. Figure 3.15 shows the BCC phase formed on the outer surface of a specimen heated for 17 hours at 1900°C.

Powder samples of $\text{UO}_2.99 \cdot 3\text{Y}_2\text{O}_3$ were heated at 1650° to 1700°C in air from 5 to 112 hours (Table 3.2). The X-ray analysis indicated trace amounts of a BCC phase present in these samples. Prior X-ray analysis indicated the powders were single-phase Rhombohedral I. Chemical analysis showed a decrease in the oxygen-to-uranium ratio from 2.99 to 2.92, but no measurable fuel loss in up to 112 hours at 1670°C. The amount of BCC phase was higher, as would be expected, in samples which volatilized some fuel at 1700°C. The phases observed were in agreement with the phase relationships presented in the section on the " $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ System."

TABLE 3.2
X-RAY DIFFRACTION AND CHEMICAL ANALYSES OF $\text{UO}_2.99 \cdot 3\text{Y}_2\text{O}_3$ POWDER
AFTER VARIOUS HEAT TREATMENTS IN AIR

Temperature, °C	Time, hr	Phases	Chemical Analysis		Theoretical Percent Uranium For $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3^a$
			Uranium, %	Oxygen-To-Uranium Ratio	
1650	5	Rh I	24.7 ± 0.1	2.98	24.7
	25	Rh I + Trace BCC	24.7 ± 0.1	2.97	24.7
	47	Rh I + Trace BCC	24.7 ± 0.1	2.97	24.7
1670	112	Rh I + Slight trace BCC	24.7 ± 0.1	2.97	24.7
1700	20	Rh I + 5% BCC	-	-	-
	40	95% Rh I + 5% BCC	24.3 ± 0.1	2.94	24.7
	60	95% Rh I + 5% BCC	24.0 ± 0.1	2.93	24.7

^aWhere x = oxygen-to-uranium ratio minus 2.

Water Vapor Corrosion Studies

Corrosion tests were conducted on $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ hexagonal tubes at 1510°C in wet air (+20°C dewpoint, 1.41 wt % H_2O). After 100 hours a weight loss of less than 0.02 percent was observed. A control specimen heated in dry air (-68°C dewpoint) showed an increase in weight of 0.03 percent.

Water vapor corrosion tests were also conducted on BeO coextruded hexagonal tubes with a 0.076 millimeter (0.003 inch) inside diameter cladding of $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$. These tests were performed by passing moist air through the tube which was radiantly heated by a tungsten heating element surrounding the outside surface of the tube. The temperature of the test sample was measured by Pt / Pt - 10Rh thermocouples embedded in the tube wall.

The mass velocity of the air for the tests was 4.37 g/sec-cm² (0.0588 lb/sec-in.²) with an inlet air temperature of 20°C and a water vapor content of 0.65 percent (+7°C dewpoint) by weight. Tests were run continuously for 134 hours and 162 hours at 1370°C.

The magnitude of material loss by water vapor corrosion was determined by water-immersion measurement techniques. This method permits local cross sectional area changes to be determined. These changes can then be directly converted into material loss data.

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Figure 3.12 and Figure 3.13 - These photomicrographs were transposed. The figure titles are correct as published.

Neg. 557

ETCHED IN WARM H_2SO_4

500 X

GRAIN SIZE - 6 MICRONS

Fig. 3.12 - Microstructure of $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ sintered in oxygen for 3 hours at 1750°C

Neg. 1296

AS-POLISHED

100 X

Fig. 3.13 - Microstructure of oxygen-sintered $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ after heating for 19 hours at 1850°C in oxygen

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Fig. 3.14—Microstructure of oxygen-sintered $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ after heating for 11 hours at 1900°C in oxygen

Fig. 3.15—Microstructure of oxygen-sintered $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ after heating for 17 hours at 1900°C in oxygen

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Previous experimental work¹⁸ on unfueled, uncoated BeO tubes showed these methods to be accurate within ± 0.5 percent. The post-test measurement of tubes in this test showed no evidence of material loss. For comparison purposes, an uncoated BeO tube under the same conditions showed a cross sectional area reduction of 4.8 percent.

Compatibility with BeO

Compatibility tests were conducted on BeO in contact with $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ at temperatures above and below the BeO- Y_2O_3 eutectic (1580°C) utilizing BeO tubes coextruded with 0.076 millimeter (0.003 inch) inside surface cladding of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition as well as pressed diffusion compacts.

Sintering studies on the coextruded tubes in an air atmosphere showed that a dense $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ cladding was formed at temperatures as low as 1550°C ; however, the BeO matrix did not densify well below 1580°C . At temperatures above the BeO- Y_2O_3 eutectic, a liquid grain boundary phase which promotes sintering forms in the BeO. However, the rate of liquid formation is very slow in an oxidizing atmosphere in the temperature range 1600° to 1650°C . At temperatures above 1650°C , liquid formation is fairly rapid and is accompanied by deterioration of the cladding and significant fuel loss.

Figure 3.16 shows the microstructure of a specimen sintered in an oxidizing atmosphere for 3 hours at 1560°C ; the BeO grain size was 10 microns. During an additional 224-hour test at 1560°C , the BeO grain size increased to 90 microns with no evidence of liquid phase formation, as shown in Figure 3.17.

Figure 3.18 shows the microstructure of a specimen sintered in an oxidizing atmosphere for 2 hours at 1600°C . A liquid phase was not detected, and the grain size of the BeO was approximately 20 microns. Continued heating for 16 hours resulted in slight liquid formation with grain size increasing to 42 microns. After a total of 82 hours at 1600°C , a definite evidence of liquid formation at the BeO grain boundaries was noted, as shown in Figure 3.19, and the grain size increased to 68 microns.

After each of the above tests, no evidence of any cladding deterioration or breakdown of the cladding - substrate bond was found. The dark line at the interface of the photomicrographs is a result of the relief polishing of the cladding.

The addition of ZrO_2 to BeO as a possible means of improving the refractoriness of the system was investigated.¹⁹ Interaction of the matrix and the cladding were studied in coextruded tubes in which 5 weight percent ZrO_2 (as a sol) was added to the BeO. High-temperature stability tests were conducted to compare the compatibility between the cladding and to compare the BeO matrix of coextruded tubes with and without the ZrO_2 addition. After sintering for 2 hours at 1600°C , the grain size was 8 microns, as shown in Figure 3.20 compared to 20 microns for a sample without the ZrO_2 addition (Figure 3.18). After 82 hours at 1600°C in dry air, grain size increased to 20 microns (Figure 3.21), compared to 68 microns for specimens without ZrO_2 addition heated under the same conditions, Figure 3.19. Petrographic examination showed the presence of cubic ZrO_2 , an indication that a portion of the Y_2O_3 was combining with the monoclinic ZrO_2 . There was also evidence of a liquid phase, assumed to be BeO- Y_2O_3 .

Analysis of coextruded tubes having $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ as cladding on BeO with and without a 5 weight percent ZrO_2 addition was made utilizing the electron probe to identify phases present in the cladding and matrix. The cladding of the BeO tube without the ZrO_2 addition was single phase, analyzing 25 percent uranium and 55 percent yttrium, which corresponds to the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition. The grain boundary phase in the BeO was a BeO- Y_2O_3 composition containing 40 to 45 percent yttrium. No uranium was detected in the BeO.

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Fig. 3.16—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ -BeO tube sintered at 1560°C for 3 hours in air

Fig. 3.17—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ -BeO tube sintered at 1560°C for 3 hours in air and heated for 224 hours at 1560°C in dry air

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Fig. 3.18—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3\text{-BeO}$ tube sintered in air for 2 hours at 1600°C

Fig. 3.19—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3\text{-BeO}$ tube sintered in air for 2 hours at 1600°C and heated in dry air for 82 hours at 1600°C

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Neg. 1778

ETCHED IN 20% HF

250 X

Fig. 3.20—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3\text{-BeO} + 5$ weight percent ZrO_2 tube sintered in air for 2 hours at 1600°C

Neg. 1780

ETCHED IN 20% HF

250 X

Fig. 3.21—Microstructure of coextruded $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3\text{-BeO} + 5$ weight percent ZrO_2 tube sintered in air for 2 hours at 1600°C and heated in dry air for 82 hours at 1600°C

Electron-probe analysis of clad tubes with the addition of 5 weight percent ZrO_2 to the BeO indicated a yttria-deficient zone in the cladding next to the BeO. The composition was 45 percent uranium and 49 percent yttrium, corresponding to $2\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$, whereas the balance of the cladding was the normal $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition. As previously observed, yttria was present in the BeO both as a BeO- Y_2O_3 grain boundary phase and in solid solution with the ZrO_2 . However, the small area of the Y_2O_3 -BeO grain boundary phase was less than the limit of resolution of the electron beam, and therefore a quantitative analysis of the yttria-containing phases was not possible. No urania was detected in the BeO.

Hexagonal BeO tubes, 0.671 centimeter (0.264 inch) across flats, were prepared with 0.076 millimeter (0.003 inch) of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ coextruded on the bore which was, in turn, dip coated with 0.051 millimeter (0.002 inch) of BeO to obtain an ID of 0.450 centimeter (0.185 inch). An as-sintered tube is shown in Figure 3.22. These tubes were bench tested in moving dry air at 1370°C for 979 hours to provide reference data for future in-pile testing at the same temperature. The tubes remained unchanged except for a slight grain growth as shown in Figure 3.23. The tubes showed no weight loss during testing.

Fuel Recovery

Since fuel reprocessing is of concern in any reactor system, a cursory evaluation of fuel reclamation was made as a feasibility study on a laboratory scale only. These preliminary studies showed that the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ cladding on the BeO fuel element has the further advantage over a dispersed-type fuel element in that the recovery and reprocessing of the fuel is greatly simplified. The fueled cladding can be removed from the BeO tube in 2 to 3 hours using warm perchloric acid resulting in a solution containing all of the fuel.

Thermal Expansion

The thermal expansion of the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ composition in both the oxidized and reduced form was measured using a cantilevered-beam, continuous-recording technique. Figure 3.24 is a plot of the percent of expansion as a function of temperature for $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ measured in air. The thermal expansion curve for BeO^{18} is also plotted in Figure 3.24 to illustrate the good match in the thermal expansion characteristics of BeO and $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$. The cantilever-beam technique was used to observe dimensional changes of hydrogen-sintered specimens ($\text{UO}_2 \cdot 2 \cdot 3\text{Y}_2\text{O}_3$) during heating from 25° to 1200°C and 1425°C in air. Figure 3.25 shows the dimensional changes that dense bodies of the $\text{UO}_2 \cdot 2 \cdot 3\text{Y}_2\text{O}_3$ composition undergo when heated in air. Table 3.3 summarizes the X-ray data for phase transitions which occurred during these experiments. The sample heated to 1200°C contracted more than the one heated to 1425°C . This is in agreement with calculated unit cell volumes for the phases present.

The sample heated to 1200°C had an oxygen-to-uranium ratio of 2.88, and the sample heated to 1425°C had an oxygen-to-uranium ratio of 2.90. Thus, the inflection in the expansion curve for the 1425°C sample above 1200°C primarily reflects cation rearrangement since the sample is almost fully oxidized by 1200°C .

The linear thermal expansion of the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ composition was measured at temperatures up to 2300°C in hydrogen by optical methods. The specimen was $\text{UO}_2 \cdot 92 \cdot 3\text{Y}_2\text{O}_3$ at the beginning of the test. The resulting curve, Figure 3.26, consists of two distinct regions with an inflection between 1200°C and 1500°C . Since the original specimen has an oxidized, single-phase rhombohedral I structure and the reduced specimen after treatment in hydrogen above 2000°C consists of two phases, BCC and FCC, these data suggest that transformation occurs in the 1200° to 1500°C region. The heating portion of the curve above 1500°C and the cooling curve show the expansion characteristics of the body in the

Fig. 3.22—Coextruded BeO-UO_{2.9}·3Y₂O₃ tube dip coated with BeO cladding and sintered for 2 hours at 1600°C in air

Fig. 3.23—Coextruded dip coated BeO-UO_{2.9}·3Y₂O₃ tube sintered for 2 hours at 1600°C in air and heated for 979 hours in dry air at 1370°C

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GE-NMPO

Fig. 3.24 – Thermal expansion of BeO and $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ in air

TABLE 3.3

PHASE CHANGE OF REDUCED $\text{UO}_{2.2} \cdot 3\text{Y}_2\text{O}_3$ THERMAL
EXPANSION SPECIMENS HEATED IN AIR FROM
25°C TO 1425°C

Temperature, °C	Oxidation State	Phase
25	Reduced	Rhombohedral I (Reduced) + Body-centered cubic (BCC)
1200	Oxidized	Rhombohedral II ^a + BCC
1425	Oxidized	Rhombohedral I (Oxidized)

^aThe rhombohedral II has been observed as an intermediate compound found during the oxidation of $2\text{UO}_{2.2} \cdot 3\text{Y}_2\text{O}_3$.

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Fig. 3.25 -- Thermal expansion curves for hydrogen-sintered samples measured in air to 1200°C and 1425°C

diphasic, reduced state. Chemical analysis of the specimen after test showed the oxygen-to-uranium ratio was 2.08. Electron probe analysis established that the composition of the BCC phase was $\text{UO}_{2+x} \cdot 6\text{Y}_2\text{O}_3$ and that of the FCC phase was $\text{UO}_{2+x} \cdot \text{Y}_2\text{O}_3$.

Figure 3.27 shows the thermal expansion as a function of temperature for a reduced $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ sample measured in hydrogen to 2300°C. Included for comparison purposes are thermal expansion curves for UO_2 and Y_2O_3 obtained under the same experimental conditions.

Thermal Conductivity

The thermal conductivity of the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ composition was measured between 750° and 1950°C in hydrogen. The measurements were made by using the radial heat flow technique on hydrogen-sintered $\text{UO}_2 \cdot 2 \cdot 3\text{Y}_2\text{O}_3$ specimens of 51-centimeter (2-inch) diameter discs, 1.3 centimeters (1/2-inch) thick, having a density of 99.5 percent of theoretical. Figure 3.28 is a plot of the thermal conductivity versus mean temperature of these speci-

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Fig. 3.26— Linear thermal expansion of oxygen-sintered sample measured in hydrogen to 2300°C

Fig. 3.27— Thermal expansion of reduced $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$, UO_2 , and Y_2O_3 measured in hydrogen

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Fig. 3.28 – Thermal conductivity versus mean temperature for $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ and UO_2

mens. The thermal conductivity (K) varied from 0.0069 cal/sec-cm-°C at a mean temperature of 750°C to 0.0052 at 1950°C. The thermal conductivity for $\text{UO}_{2.01}$ was measured to 2200°C, and these data in addition to Kingery, et al.,²⁰ are included here for comparison.

Densities

The theoretical densities of the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ composition were determined from X-ray data for both the oxidized state ($\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ - Rh I phase) and the reduced state ($\text{UO}_{2.2} \cdot 3\text{Y}_2\text{O}_3$ - 28% Rh I and 72% FCC phases). The values are 6.00 gm/cm³ and 5.867 gm/cm³, respectively.

Electrical Properties

Measurements of the electrical resistivity of the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ composition were made on both oxidized (oxygen-sintered) and reduced (hydrogen-sintered) specimens in a helium atmosphere. Resistivity was calculated from the measured voltage drop across a specimen carrying a 60-cycle a-c current.

The experimental results are plotted in Figure 3.29. The data indicate that the oxidized material has a higher resistivity than the reduced material for temperatures below 1700°C. However, at higher temperatures, appreciable reduction of the oxidized material occurs by evolution of oxygen which is swept away by the helium atmosphere. Under these circumstances, the resistivity of the oxidized specimen approaches that of the reduced material. Chemical analysis confirms the reduction of the oxidized specimen, showing a decrease in the oxygen-to-uranium ratio from 2.92 to 2.18. The resistivity of both samples at 2200°C was 0.55 ohm-cm.

A cell was constructed to measure the electrical conductivity and to determine the conduction mechanism for various compositions in the $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ system in an oxidizing atmosphere. A schematic diagram of the cell is shown in Figure 3.30. The charge-carrying species in a conductor may be identified as ionic by means of electrolytic cell measurement. A simple method consists of using the material under study as a solid electrolyte

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to separate two electrode reactions. For an oxide, a cell of the type $O_2(P)$, Pt: MO: Pt, $O_2(P')$ may be used, where P and P' refer to different partial pressures of oxygen maintained at the respective electrodes. If the oxide (MO) is an ionic conductor, the potential developed will be that shown in Equation (3.1):

$$E_i = \frac{2.3 RT}{4F} \log \frac{P'}{P} \quad (3.1)$$

Fig. 3.29— Resistivity as a function of temperature for oxidized and reduced $UO_{2+x} \cdot 3Y_2O_3$ measured in helium

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If the conductivity is partially ionic and partially electronic, the ionic transport number (t_i) will be given by E_p/E_1 , where E_p is the measured emf developed and E_1 is the theoretical emf calculated from Equation (3.1). Thus, ionic and electronic contributions to the total conductivity may be determined.

Fig. 3.30— Schematic diagram of apparatus for electrical resistivity and transport number measurements

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A preliminary run was conducted on polycrystalline cubic ZrO_2 (19.6 mole % CaO), which is essentially a completely ionic conductor. The test samples consisted of 2-centimeter-diameter wafers, 0.127 centimeter thick with the electrical contact through porous platinum electrodes, 1 centimeter in diameter. The ionic transport numbers were measured by using air and oxygen at opposite electrodes. Interchanging the gases on the electrodes showed that the cell was reversible. Ionic transport numbers of 0.90 were measured between 1000°C and 1400°C, 10 percent below the theoretical value for a purely ionic conductor. This low value is possibly a result of some small cracks in the sample which allowed some gas leakage.

Similar measurements were made on samples of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ and $2\text{UO}_2 \cdot 95 \cdot 3\text{Y}_2\text{O}_3$. This latter sample was about 50 percent Rh I and 50 percent FCC. No measurable emf was obtained for the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition up to 1500°C using oxygen versus air, air versus CO_2 , and oxygen versus CO_2 . Similarly, no emf was observed for the $2\text{UO}_2 \cdot 95 \cdot 3\text{Y}_2\text{O}_3$ composition for temperatures up to 900°C. Examination showed that the samples were sound after the measurements. Consequently, it is concluded that these materials are essentially electronic conductors with little or no ionic contribution in these temperature ranges.

The electrical conductivity of the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ and the $2\text{UO}_2 \cdot 95 \cdot 3\text{Y}_2\text{O}_3$ compositions was measured in oxygen and air to 1500°C and 1000°C, respectively. The results are plotted in Figure 3.31. Both a-c and d-c measurements of the conductivity were made. Polarization effects, resulting in an increase in electrical resistance with time, were observed during d-c measurements. Consequently, the data in Figure 3.31 were plotted from a-c measurements employing an impedance bridge with 1000 cycles per second, a-c current. The conductivity of the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ composition increases from 2.8×10^{-5} (ohm-cm) $^{-1}$ at 300°C to 9×10^{-3} (ohm-cm) $^{-1}$ at 1480°C. The activation energy for this process is 0.80 ev, comparable to the activation energy for the extrinsic range for UO_{2+x} as reported by Williardson et al.²¹ The conductivity for the $2\text{UO}_2 \cdot 95 \cdot 3\text{Y}_2\text{O}_3$ composition increases from 3.5×10^{-4} (ohm-cm) $^{-1}$ at 150°C to 3.25×10^{-2} (ohm-cm) $^{-1}$ at 1000°C, with an activation energy of 0.60 ev.

Electrical conductivity and transport numbers were measured on the $2\text{UO}_3 \cdot x \cdot 3\text{Y}_2\text{O}_3$ composition to 1500°C in air and in oxygen atmospheres. The measurements to 1500°C for the mixed phase sample are plotted in Figures 3.32 and 3.33. A second sample (B) of the same composition as specimen A was prepared as face-centered-cubic phase (FCC) solid solution; the data for this sample to 1500°C are shown in Figures 3.34 and 3.35.

The X-ray and chemical analyses data for the two specimens of the $2\text{UO}_3 \cdot x \cdot 3\text{Y}_2\text{O}_3$ compositions are given in Table 3.4.

The transport measurements given in Figures 3.33 and 3.35 show that there is a partial ionic contribution to the conductivity which amounts to about 5 percent at 1000°C and reaches about 14 percent at 1500°C.

The conductivity measurements to 1500°C on the specimen A (50% FCC, 50% Rh I) are shown in Figure 3.32. From 1000°C to 1500°C, there is a complex region in which conductivity decreases with increasing temperature. Discontinuous behavior of this kind usually signifies a transition region from extrinsic to intrinsic mode of conductivity in semiconductors. This is, however, the temperature range in which transport measurements indicate that mixed conductivity becomes a significant factor. Thus the region of discontinuous behavior probably represents a region of complexity in which there is decreasing electronic conductivity and increasing ionic contributions to the total conductivity. Further studies in oxidizing atmospheres at temperatures above 1500°C are required to clarify the mechanisms involved.

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Fig. 3.31 – Electrical conductivity as a function of reciprocal temperature for two compositions in the $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ system

TABLE 3.4		
X-RAY DIFFRACTION AND CHEMICAL ANALYSES OF CONDUCTIVITY SPECIMENS		
Sample	Phases Present	Oxygen-To-Uranium Ratio
A	50% RhI +	2.94
	50% FCC	
B	100% FCC	3.00

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Fig. 3.32—Electrical conductivity versus reciprocal temperature for $2UO_{3-x} \cdot 3Y_2O_3$ (initially $\sim 50\%$ FCC— 50% Rh I)

Fig. 3.33—Ionic conductivity as a function of temperature for $2UO_{3-x} \cdot 3Y_2O_3$ (initially 50% FCC, 50% Rh I)

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Fig. 3.34—Electrical conductivity versus reciprocal temperature for $2UO_{3-x} \cdot 3Y_2O_3$ (initially 100% FCC)

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Fig. 3.35—Ionic conductivity as a function of temperature for $2\text{UO}_{3-x} \cdot 3\text{Y}_2\text{O}_3$ (initially 100% FCC)

An activation energy of 0.6 eV was calculated assuming the relationship, $\sigma = A \exp(-E/2kT)$, for the straight line portion of the $\log \sigma$ versus $1/T$ curve. Activation energies of this magnitude are typical of extrinsic conductivity. For example, typical activation energies for UO_{2+x} range from 0.4 to 0.9 eV²¹ for the extrinsic semiconductor region. The activation energy for intrinsic semiconductor in similar oxide systems generally is of the order of several electron volts; the activation energy for UO_{2+x} , for instance, is approximately 4.0 eV for intrinsic semiconductor.²¹

Figure 3.34 shows the plot of $\log \sigma$ versus $1/T$ for the face-centered-cubic specimen. Three distinct regions are observed in this plot. Between 200°C and approximately 600°C, the curve is linear as the temperature is increased. The activation energy for the conduction process in this range is 0.8 eV. At approximately 600°C, there is a break in the curve and the rate of increase in conductivity is significantly higher. The "activation-energy" over this range is 2.10 eV. Above 780°C, the curvature previously discussed for specimen A is also observed. Thermogravimetric analyses of the $2\text{UO}_{3-x} \cdot 3\text{Y}_2\text{O}_3$ composition (Figure 3.36) indicates that the region of rapid change in conductivity corresponds to the temperature range (~600°C) at which the fluorite solid solution initially undergoes significant reversible oxygen dissociation.

Oxygen dissociation effects are not observed as readily in the Rh I structure, which appears to be an ordered structure which does not readily dissociate upon heating in air or oxygen. The FCC structure, on the other hand, gives off oxygen on heating in air or oxygen and consequently would be expected to show some marked changes in electrical properties if oxygen deficiencies (i.e., defects or vacancies in the oxygen sublattice)

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Fig. 3.36—Thermogravimetric analysis of $2\text{UO}_{3-x}\cdot 3\text{Y}_2\text{O}_3$ (FCC) showing reversible oxygen dissociation upon thermal cycling in air

contribute significantly to the extrinsic semiconducting properties of this system. This effect is observed in Figure 3.34 of the $2\text{UO}_{3-x}\cdot 3\text{Y}_2\text{O}_3$ composition where, as indicated above, the break in the $\log \sigma$ versus $1/T$ curve corresponds to the temperature region ($\sim 600^\circ\text{C}$) in which appreciable oxygen dissociation occurs. This temperature range is well below that at which appreciable cation mobility is observed in phase equilibria studies; hence, the behavior appears to be associated with the degree of oxygen dissociation. Fully oxidized $2\text{UO}_3\cdot 3\text{Y}_2\text{O}_3$ has an oxygen-to-metal ratio of 15:8 or 1.875. This ratio is sufficiently reduced when the temperature exceeds approximately 600°C to introduce further oxygen vacancies in the oxygen sublattice with corresponding enhanced electrical conductivity. This effect was found to be reversible.

No such enhanced conductivity effect was observed in either the $\text{UO}_3\cdot 3\text{Y}_2\text{O}_3$ composition (100% Rh I) or in the initial measurement on the $2\text{UO}_{3-x}\cdot 3\text{Y}_2\text{O}_3$ sample (50% Rh I - 50% FCC). These results are in agreement with the oxygen dissociation effects discussed above since thermogravimetric studies¹⁶ show the rhombohedral phase (Rh I) does not undergo oxygen dissociation to the degree observed in the fluorite solid solution.

Vapor Pressure

Transpiration measurements were made to establish the vapor pressure of UO_3 over $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ as a function of temperature, using oxygen and air as carrier gases. These data are shown in Figure 3.37. Vapor pressures were found to range from 8.04×10^{-9} atmosphere at 1400°C to 1.78×10^{-6} atmosphere at 1710°C . The upper limit of the vapor pressure of yttria was found to be 10^{-9} atmosphere at 1700°C . The vapor pressure of UO_3 above U_3O_8 in air or oxygen varies from 4×10^{-4} atmosphere at 1540°C to 1×10^{-6} atmosphere at 1200°C .

Heat Capacity

Heat capacity measurements of the $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ composition were made to 2000°C by employing a drop technique in conjunction with an adiabatic calorimeter. Enthalpy data obtained on both oxidized and reduced specimens are plotted as a function of temperature in Figure 3.38. These data show that, as expected, the heat capacity (C_p) is not appreci-

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Fig. 3.37 - Vapor pressure of UO_3 over $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$

ably influenced by the oxidation state of the material. The following equations give the enthalpy - temperature and heat capacity - temperature relationships for these data.

$$H_{298}^T = -31.04 + 0.101T + 5.97 \times 10^{-6} T^2 + 2.98 \times 10^{-9} T^3, (T = ^\circ\text{K}) \quad (3.2)$$

Thus,

$$C_p = 0.101 + 11.94 \times 10^{-6} T + 8.94 \times 10^{-9} T^2 \quad (3.3)$$

The maximum deviation of the experimental data from that calculated using Equation (3.3) was 2.13 percent. Except for two points in the lower temperature range ($\sim 530^\circ\text{K}$), agreement was within 1 percent. Table 3.5 tabulates some values for both mean $C_p(H_{298}^T/\Delta T)$ and C_p calculated from Equations (3.2) and (3.3), respectively.

The same experimental technique was used to measure the heat capacity of UO_2 between 930°C and 1925°C . The data for these experiments are plotted in Figure 3.38. Table 3.6 summarizes the mean C_p for these data.

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Fig. 3.38—Enthalpy of $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ and UO_2 as a function of temperature

TABLE 3.5

HEAT CAPACITY OF $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$

Temperature, °C	Heat Capacity (C_p), cal/g-°C	Mean Heat Capacity ($\bar{C}_p$), cal/g-°C
200	0.109	0.106
400	0.113	0.108
600	0.118	0.111
800	0.124	0.114
1000	0.131	0.116
1200	0.138	0.120
1400	0.146	0.123
1600	0.154	0.126
1800	0.164	0.130
2000	0.174	0.134

TABLE 3.6

HEAT CAPACITY OF UO_2

Temperature, °C	Mean Specific Heat ($\bar{C}_p$), cal/g-°C
929	0.0724
1030	0.0736
1183	0.0744
1327	0.0743
1454	0.0760
1606	0.0769
1702	0.0783
1800	0.0788
1924	0.0810

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3.3 MECHANICAL PROPERTIES

Modulus of Rupture of $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$

Modulus of rupture tests were made to evaluate the strength properties of $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ in the oxidized state ($x = 0.9$) and the reduced state ($x = 0.2$). The specimens consisted of extruded and sintered round rods 8.9 to 12.7 centimeters (3.5 to 5 inches) in length, centerless ground to 0.610 centimeter (0.240 inch) in diameter. The rods were broken at room temperature by using a 4-point loading on a 7.6-centimeter (3-inch) span. Additional data were obtained utilizing the broken sections on a 4.4- or 3.2-centimeter (1-3/4- or 1-1/4-inch) span with either a 3- or 4-point loading. The ram travel was 0.15 centimeter (0.060 inch) per minute.

A statistical analysis of the data (Table 3.7) showed that the oxygen-sintered samples had a higher modulus of rupture strength than the hydrogen-sintered samples. Table 3.7 shows that a 3-point loading produced consistently higher values than a 4-point loading in agreement with previous work on BeO .²³ It should be noted that decreasing the span yielded higher apparent modulus of rupture values.

A portion of the rods that were oxygen sintered was reduced in hydrogen at 1700°C for 48 hours. Three of these reduced samples were again oxidized by heating in air for 24 hours at 1450°C. The modulus of rupture data (Table 3.7) indicate a possible small decrease in strength in the reduced specimens.

Modulus of rupture measurements were also made on $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ specimens, 0.51 by 0.51 by 5.08 centimeters, sintered in oxygen to 99.7 to 99.8 percent of theoretical density. Measurements made at room temperature, 1000°, 1250°, and 1500°C in air are summarized in Table 3.8. These measurements were made using a 3-point loading on a 4.44-centimeter span with a 0.20-centimeter head travel per minute.

Microscopic examination of the fracture edges of modulus of rupture specimens indicates that transgranular fracture occurs both in the oxidized and reduced specimens. A typical fracture is shown in Figure 3.39. Figures 3.40 and 3.41, show the fracture patterns of BeO and Al_2O_3 , respectively, and are included for comparison purposes. Both of these latter materials show greater strength, and the photomicrographs show less transgranular fracture. All modulus of rupture specimens were examined by Zyglo and radiographic methods and found to be free of fissures and voids prior to breaking.

Room-temperature and elevated-temperature modulus of rupture tests were conducted on coextruded BeO hexagonal tubes with 0.076-centimeter (0.003-inch) inside diameter cladding of $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ sintered in air at 1600°C for 2 hours. The tube dimensions were 0.67 centimeter (0.264 inch) across flats with a 0.48-centimeter (0.189-inch) inside diameter. The tubes were broken with a 4-point loading on 7.6-centimeter (3-inch) span with 0.15-centimeter (0.060 inch) per minute beam travel. Eleven tubes were tested at room temperature and had an average modulus of rupture of 1850 kg/cm² (26,300 psi) with a standard deviation of 176 kg/cm² (2,500 psi). Nine tubes that were tested at 1370°C had an average modulus of rupture of 1322 kg/cm² (18,800 psi) with a 112 kg/cm² (1,600 psi) standard deviation.

Elastic Properties

The temperature dependence of the dynamic modulus was measured from room temperature to 1510°C for the $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ composition. These data are presented in Figures 3.42, 3.43, and 3.44 and show that both the dynamic modulus of elasticity and dynamic shear modulus decrease with temperature. Calculated Poisson's ratio remains essentially constant at 0.3. The test specimen was 10 centimeters (4 inches) long and 0.63 centimeter (1/4 inch) in diameter and was suspended in the furnace on two platinum wire loops at the

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TABLE 3.7

MODULUS OF RUPTURE OF OXYGEN- AND HYDROGEN-SINTERED $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ COMPOSITION
AND OF OXYGEN-SINTERED, REDUCED, AND REOXIDIZED SAMPLES

Test Condition		Oxygen-Sintered $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ 1750°C For 3 Hours			Hydrogen-Sintered $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ 1700°C For 12 Hours			Hydrogen-Reduced $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ 1700°C For 48 Hours			Air-Reoxidized $\text{UO}_{2+x}\cdot 3\text{Y}_2\text{O}_3$ 1450°C For 24 Hours		
Loading Point	Span, in.	No. Of Samples Tested	Average, kg/cm ²	Standard Deviation	No. Of Samples Tested	Average, kg/cm ²	Standard Deviation	No. Of Samples Tested	Average, kg/cm ²	Standard Deviation	No. Of Samples Tested	Average, kg/cm ²	Standard Deviation
4	3	23	940	100	16	749	116						
4	1.75	15	993	83	11	865	86						
3	1.75	26	1044	120	6	903	193						
3	1.25	19	1132	80	15	984	124						
4	3							8	724	204	3	808	108
3	1.75							9	963	234	3	1005	4
3	1.25							8	1083	199	2	1111	30

Fig. 3.39—Transgranular fracture of $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$, sintered in O_2 for 3 hours at 1750°C

Neg. 694

ETCHED IN WARM
 H_2SO_4 SOLUTION

500 X

Fig. 3.40—Fracture pattern of UOX-grade beryllia plus 0.5 weight percent MgO , sintered in hydrogen for 3 hours at 1540°C

Neg. 692

ETCHED IN WARM
50% HF SOLUTION

500 X

Fig. 3.41—Fracture pattern of alumina (Linde A) plus 0.25 weight percent MgO , sintered in hydrogen for 10 hours at 1700°C

Neg. 693

AS POLISHED

500 X

TABLE 3.8
MODULUS OF RUPTURE OF $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ AT VARIOUS TEMPERATURES

Number of Specimens	Temperature, °C	Average Modulus Of Rupture, kg/cm^2	Spread, kg/cm^2
18	Room Temperature	1380	700 - 1830
4	1000	1360	1170 - 1660
4	1250	1260	800 - 1590
4	1500	1650	1450 - 1940

Fig. 3.42 – Dynamic modulus of elasticity versus temperature for $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$

Fig. 3.43 – Dynamic shear modulus versus temperature for $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$

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Fig. 3.44 – Calculated Poisson's ratio versus temperature for $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$

nodal points. One platinum wire was attached to an external crystal exciter and the other loop to an external crystal pickup. This arrangement permitted simultaneous measurement of the fundamental transverse and torsional frequencies.

Compressive Creep

Compressive creep measurements were made on $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ samples 0.5 by 0.5 by 2.5 centimeters (0.2 by 0.2 by 1.0 inch) having a density of 99.7 percent of theoretical. The total deformation after 100 hours at 1540°C in air was 0.43 percent for a load of 8.8 kg/cm² (125 psi) and 0.50 percent for a load of 17.6 kg/cm² (250 psi).

Thermal Stress Resistance

Previous experience showed that a BeO homogeneous dispersion-type fuel element generally fails because of residual stresses induced upon cooling.²⁴ By applying the fuel as an inside surface cladding to the BeO, however, thermal gradients are greatly reduced. Thermal stress calculations were made comparing these two fuel element concepts at a power level of 150 g-cal/cm²-sec (10 Btu/in.²-sec). The calculations (based on tube dimensions of 0.670 centimeter across flats, a 0.480-centimeter bore, and a 0.008-centimeter-thick cladding) are summarized in Table 3.9 and illustrate the marked advantage of concentrating the fuel as a cladding on the BeO. By concentrating the fuel at the surface, the important residual stresses are reduced from 1139 to 41 kg/cm² and elastic stress from 429 to 33 kg/cm².

Transient test methods^{24, 25} (thermal shock) were utilized to test the $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ -clad BeO tubes because of the experimental difficulty of operating a non-nuclear steady-state thermal stress test that would simulate actual operating conditions of the fuel element; i. e., internal power generation uniformly distributed throughout the cladding only with all heat removed from the bore. Thermal stresses were imposed by heating the tube to equilibrium temperature and then passing room temperature air through the bore of the tube. Heat removal rates were determined by readings from thermocouples imbedded in the tube with measurements recorded on a high-response self-balancing recording potentiometer. The stress calculations (described previously²⁵) assumed elastic behavior.

These tests showed that at 1370°C a stress in the BeO portion of 914 kg/cm² (13,000 psi) was required to produce cracking, while at 1480°C a BeO stress level of 562 to 703 kg/cm² (8,000 to 10,000 psi) produced cracking after repeated cycling. These values are greatly in excess of the calculated operating stresses as presented in Table 3.9.

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TABLE 3.9
COMPARISON OF CALCULATED STRESSES IN THREE TYPES OF FUEL ELEMENTS
FOR A CONSTANT HEAT REMOVAL RATE OF 150 g-cal/cm²-sec

	Unclad Fueled BeO	ZrO ₂ -Clad Fueled BeO		UO _{2.9} ·3Y ₂ O ₃ -Clad BeO	
	Matrix	Matrix	Clad	Matrix	Clad
Temperature gradient, °C	18.1	16.3	11.0	0.6	9.5
Maximum elastic stress, kg/cm ²	562 T ^a	429 T	703 T	33 T	155 T
Maximum residual stress, kg/cm ²	1033 T	1139 T	337 C ^b	41 T	260 T

^aT - tensile

^bC - compressive

There was no indication of failure of the cladding or cladding-matrix interface which is confirmation of the excellent match of expansion characteristics of BeO and UO_{2.9}·3Y₂O₃ reported in an earlier section.

Analysis and experiments in thermal stress have used cracks as a method of determining the severity of thermal stress, although it must be recognized that cracking, especially the type detectable only by fluorescent dye penetrants, would not necessarily constitute failure of a fuel element to perform its desired function.

3.4 IRRADIATION TESTS

Two pellets of UO_{2.9}·3Y₂O₃ composition using uranium of 0.35 weight percent U²³⁵ enrichment were irradiated in the ORR at a maximum temperature of 400°C to determine the effects of fast neutrons on microstructure, phase stability, and physical integrity of dense bodies of this composition. The total dosage of fast neutrons (> 1 Mev) was 1020 nvt. No changes in specimen dimensions or density occurred during irradiation. Microscopic comparison of as-polished sections of both irradiated and unirradiated samples revealed no observable cracks or other radiation-induced flaws. Samples etched in warm H₂SO₄ revealed a general overall tendency for the irradiated specimen to etch more heavily along grain boundaries than the unirradiated control specimen. Other than this etching effect, however, there were no detectable differences in grain size or microstructure between specimens.

The X-ray diffraction analyses indicate that a crystallographic phase change from the ordered Rh I structure to a FCC structure occurred during irradiation. This change occurred without cracking or other physical disruption of the irradiated specimens.

Further irradiation tests to evaluate the fission product retention characteristics and effects of high burnup on stability of this fuel composition in a BeO-clad, coextruded tube are being conducted under Task 57068.

4. SUMMARY AND CONCLUSIONS

The work performed during this program resulted in a tentative phase diagram for the $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ system for temperatures up to 1700°C . Four phases were identified in the system at temperatures between 1000° and 1700°C : (1) U_3O_8 ; (2) a face-centered cubic solid solution; (3) a body-centered cubic solid solution; and (4) a rhombohedral phase of the composition $(\text{U}, \text{Y})_7\text{O}_{12}$ ranging from 52.5 to 75 mole percent Y_2O_3 . The rhombohedral phase oxidizes to a second rhombohedral phase with a nominal composition $(\text{U}, \text{Y})_8\text{O}_{15}$ at temperatures below 1000°C . This phase transforms to a FCC phase after heating in air above 1000°C . The solubility of UO_2 in the BCC phase is about 14 mole percent between 1000° and 1700°C but decreases to 0 mole percent as the uranium approaches the hexavalent oxidation state. The solubility of Y_2O_3 in the FCC solid solution ranges from 0 to 50 mole percent Y_2O_3 under reducing conditions and from 33 to 60 mole percent Y_2O_3 under oxidizing conditions at 1000°C .

At temperatures above 1000°C , the FCC solid solution is limited by a filled fluorite lattice of composition $(\text{U}, \text{Y})\text{O}_2$. Oxidation at low temperatures ($< 300^\circ\text{C}$) permits additional oxygen to be retained in the structure to a composition approaching $(\text{U}, \text{Y})\text{O}_{2.25}$.

Fabrication of the $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ composition has been straightforward. The material sinters to 99.5 percent of theoretical when the particle size of the starting powder is generally less than 5 microns in diameter. It has been cold-formed by pressing and by extrusion including co-extrusion with BeO.

The thermal stability of $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ in an oxidizing atmosphere is excellent as compared to other UO_2 carrying compositions. The material remains unchanged in air to 1700°C for times up to 500 hours. Longer times at this temperature and correspondingly shorter times at higher temperatures in air causes the material to lose uranium as UO_3 , in agreement with the measured vapor pressure of UO_3 over the material.

The coextrusion of $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ as a cladding on the inside diameter of BeO tubes shows that the material has potential for use as a high specific powder self-moderating fuel element. BeO was applied as a cladding to this fuel to minimize fission product release. It is to be noted that this sandwich-type fuel element of brittle materials is possible since the thermal expansion of $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ is very nearly the same as that for BeO.

The physical and mechanical properties of $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ are similar to those of UO_2 . The electrical conductance shows that the material is essentially an electronic conductor with possibly some ionic contribution at high temperatures. The modulus of rupture strength measurements show that $\text{UO}_2.9 \cdot 3\text{Y}_2\text{O}_3$ is somewhat stronger than the same composition in the reduced state of $\text{UO}_2.2 \cdot 3\text{Y}_2\text{O}_3$. Reoxidation, however, restores the material to about the original strength.

The results of this evaluation program indicate that the $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ fuel composition shows promise for application in reactor systems operating for several thousand hours in the temperature range from 1500° to 1700°C . Of particular interest is the fact that this

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composition is the only known high-temperature fuel material with such stability, being capable of operating in both oxidizing and reducing atmospheres and cycling between oxidizing and reducing atmospheres without catastrophic changes in strength or physical integrity. Furthermore, the $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ fuel composition as an internal fuel cladding on a tubular BeO element shows particular promise for high specific power reactor applications.

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