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PHASE RELATIONSHIPS IN THE SYSTEM
URANIUM OXIDE-LANTHANUM OXIDE

by

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
INTRODUCTION.	5
SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE . . .	8
RESULTS AND DISCUSSION.	10
SUMMARY	28
BIBLIOGRAPHY.	29

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Lattice Parameters for Urania-Lanthana Solid Solutions. . . .	10
2.	Cubic Fluorite Solubility Limits for Urania-Lanthana Compositions.	12
3.	Differences in Microstructure for High-lanthana Compositions Sintered at 1675°C for 4 Hours in Combustion Furnace. .	14
4.	Differences in Microstructure for High-lanthana Compositions Sintered in Hydrogen at 1600°C for 4 Hours.	15
5.	Differences in Microstructure for High-urania Compositions Sintered at 1675°C for 4 Hours in a Combustion Furnace. . . .	16
6.	Calculated Oxygen-to-metal Atom Ratios for Urania-Lanthana Compositions	17
7.	Effect of Stoichiometry on the Lattice Parameter for a $U_{0.5}La_{0.5}O_{1.75+x}$ Solid Solution.	18
8.	Oxygen-to-metal Atom Ratios for Urania-Lanthana Compositions Sintered at 1675°C for 4 Hours in Air.	19
9.	Microstructures of Urania-Lanthana Specimens Sintered in a Combustion Furnace at 1675°C for 4 Hours.	20
10.	The Effect of Time on Microstructure of 20 Mole % UO_2 80 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C	21
11.	The Effect of Time on Microstructure of 30 Mole % UO_2 70 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C	22
12.	The Effect of Time on Microstructure of 40 Mole % UO_2 60 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C	23
13.	The Effect of Time on Microstructure of 60 Mole % UO_2 40 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C	24
14.	The Effect of Time on Microstructure of 80 Mole % UO_2 20 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C	25
15.	Effect of Composition on Weight Loss for Urania-Lanthana Solid Solutions Subjected to Combustion Gases at 1675°C. . . .	26
16.	Surface Porosities for Urania-Lanthana Specimens Subjected to Combustion Gases at 1675°C for 310 Hours	27

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Several Binary Oxide Systems of Uranium Exhibiting Solid Solubility	6
II.	Experimental Environments Used for Phase Studies in the System Lanthana-Urania	8
III.	Base Compositions of Urania-Lanthana Solid Solutions Sintered at 1650°C in Air for 2 Hours.	10
IV.	X-ray Data and Chemical Analyses	11
V.	Lattice Parameters and Oxygen-to-metal (O/M) Ratios for $U_{0.5}La_{0.5}O_{1.75+x}$ Compositions	18
VI.	Data for Urania-Lanthana Specimens Subjected to Combustion Gases at 1675°C	26

PHASE RELATIONSHIPS IN THE SYSTEM URANIUM OXIDE-LANTHANUM OXIDE

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ABSTRACT

Urania-lanthana compositions were studied by X-ray diffraction, chemical analysis, and polished-section techniques to determine cubic fluorite solubility, lattice parameter values, stoichiometry, and microstructure. An appreciable variation in fluorite lattice parameter with composition existed for vacuum, hydrogen, and oxidizing heat treatments. The volatility behavior of urania-lanthana solid solutions was investigated by heating for extended time intervals in an oxidizing atmosphere.

INTRODUCTION

Interest in uranium oxide as a nuclear fuel is increasing because of the high melting point and irradiation performance. Uranium dioxide, however, is susceptible to oxidation, and exposure at moderate temperatures to slightly oxidizing atmospheres results in the eventual formation of U_3O_8 . This oxidation causes a structural change, accompanied by a large volume expansion, from cubic fluorite UO_2 to orthorhombic U_3O_8 ($UO_{2.67}$). Slightly oxidized or nonstoichiometric UO_{2+x} also exhibits an appreciable vapor pressure at temperatures in excess of $1200^\circ C$ ⁽¹⁾ and has shown inferior fission product retention and irradiation stability⁽²⁾ when compared with stoichiometric UO_2 .

Urania-containing binary oxide systems in which extensive solid solutions are formed may retard or inhibit this oxidation. While the addition of a nonfissionable material would considerably dilute the fuel concentration, it would be justified if enhancement of certain fuel properties were realized. The work of Anderson *et al.*,⁽³⁾ and of Hund and Peetz⁽⁴⁾ has indicated that the oxidation stability of urania may be improved by the addition of various metal oxides. A number of elements whose oxides have been reported to form fluorite solid solutions with UO_2 and $UO_{2.67}$ are listed in Table I.

Table I

SEVERAL BINARY OXIDE SYSTEMS OF URANIUM
EXHIBITING SOLID SOLUBILITY*

Valency Group	Element	Ionic Radius (Å)	Reported Solubility Limits of Additive, m/o	
			Reduced UO ₂	Oxidized UO _{2+x}
II	Mg	0.65	None	ND
	Ca	0.94	0-47	ND
III	Sc	0.68	None	ND
	Y	0.88	0-78	30-65
	La	1.04	0-52	33-70
	Nd	0.99	0-78	29-66
IV	Zr	0.77	0-40, 0-15	ND
	Th	0.99	0-100	30-100
	Pu	0.90	0-100	ND?
	Ce	0.92	0-100	40-100

*Ionic radii from Zachariasen [W. H. Zachariasen, "Crystal Chemistry of the 5f Elements," Chapter 18, pp. 769-96 in The Actinide Elements, National Nuclear Energy Ser., Div. IV, Plutonium Project Record, Vol. 14a (G. T. Seaborg, J. J. Katz, and Manning) McGraw-Hill Book Co., Inc., New York, (1954)]. Uranium ionic radii: U⁴⁺, 0.93 Å; U⁶⁺, 0.83 Å. ND, fluorite solubility known; limits, however, not determined.

The various investigations of the binary oxide systems containing uranium oxide fall into two general experimental categories: (1) work on oxidized solid solutions prepared by reacting codigested nitrates⁽⁴⁾ or mixed oxides^(5,6) in air at elevated temperatures, and (2) work on reduced solid solutions prepared by reacting the oxide additive with UO₂ under controlled atmospheric conditions.⁽⁶⁻⁸⁾ These investigations have shown that several binary systems have fluorite structures which are stable in both the "reduced" and "oxidized" states.

From the information available, several generalizations can be made. The oxides of trivalent and tetravalent elements having fluorite or related types of structures form extensive regions of solid solution with the uranium oxides. The oxides of the heavier divalent elements also form solid solutions with uranium oxide, but to a lesser extent than the trivalent elements. Solid solutions with the divalent elements are usually

formed only under carefully controlled conditions. The fluorite-type solid solutions formed with uranium oxide appear to have intact cation substructures whether they are in the reduced or oxidized state. This variation in stoichiometry seems to be accommodated by anion vacancies or interstitials within the fluorite cell.

The oxides of tetravalent elements appear to form solid solutions with UO_2 with an oxygen-to-metal atom ratio of 2. The oxidation of these stoichiometric solid solutions or the reaction of the tetravalent oxide with U_3O_8 would result in oxygen-excess fluorite structures. An analogous situation for the reaction of trivalent metal oxides with UO_2 under controlled atmospheric conditions would result in oxygen-deficient fluorite structures. Subsequent oxidation of these reduced compositions may or may not result in oxygen-excess compositions. The stoichiometry in this case would depend on the trivalent oxide concentration and the oxidation state of the uranium constituent.

Hund and Peetz⁽⁴⁾ investigated U_2O_3 - La_2O_3 compositions which were prepared by air ignition at 1200°C of codigested La^{+3} and U^{+6} nitrates. Solubility limits of 33 to 70 m/o La_2O_3 in uranium oxide were reported for these oxidized compositions. A transformation of the normally hexagonal A-type structure of La_2O_3 to the cubic C-type rare earth structure caused by the formation of the urania solid solution was also observed. Wilson⁽⁷⁾ prepared UO_2 - La_2O_3 solid solutions by sintering mixtures of UO_2 and La_2O_3 in vacuo at 1750°C . Fluorite-type solid solutions were reported to exist up to approximately 52 m/o La_2O_3 . Subsequent oxidation at elevated temperatures of these reduced solid solutions resulted in a shrinkage of the unit cell to values close to those reported by Hund and Peetz.⁽⁴⁾ Accurate analyses for oxygen concentrations in the urania-lanthana compositions were not reported in these investigations.

This investigation was concerned with the phase relationships of lanthana-urania compositions which were subjected to a variety of experimental environments. Lanthanum oxide was selected because its chemical and structural properties are similar to the other rare earths, yttria and scandia. The generalities of this system may be useful in predicting or evaluating the behavior of other urania systems containing trivalent oxide additives. Lanthana may also be a suitable additive to urania for nuclear fuels since: (1) it has one of the lowest neutron cross sections (8.9b) among the rare earths, (2) it has been shown to form an extensive series of solid solutions with the uranium oxides, and (3) it is one of the more abundant rare earths.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The materials used in this investigation were U_3O_8^* and $\text{La}_2\text{O}_3^{**}$. These materials were calcined at 800°C for 5 hr, removed from the furnace, and allowed to cool to room temperature. Mixtures containing from 20 to 93 m/o La_2O_3 were weighed immediately after cooling. The mixtures were blended by dry milling in rubber-lined mills for 3 hr, and were then placed in platinum crucibles and air calcined at 1650°C for 2 hr. Sinterable powders were produced from the calcined compositions by dry grinding in rubber-lined mills for 16 hr. After grinding, the powdered compositions were calcined in air at 700°C for 16 hr to eliminate moisture and rubber contamination.

Powders of each composition were compacted isostatically without binder at $3,500 \text{ kg/cm}^2$. Compacts of each composition were placed in platinum boats and sintered in a gas-fired furnace in an oxidizing environment at 1675°C for 4 hr. Other compacts of each composition were sintered in a hydrogen atmosphere at 1600°C for 4 hr and at 1750°C for 21 hr. Three additional compositions: UO_2 , UO_2 -6 m/o La_2O_3 , and UO_2 -10 m/o La_2O_3 , were also sintered in hydrogen at 1750°C for 21 hr. The experimental environments to which the lanthana-urania compositions were subjected in these phase studies are shown in Table II.

Table II

EXPERIMENTAL ENVIRONMENTS USED FOR PHASE STUDIES IN THE SYSTEM LANTHANA-URANIA

Experimental Environment			Type Sample Used
Atmosphere	Temp ($^\circ\text{C}$)	Time (hr)	
Oxidizing	1650	2	Calcined Powders Sintered Compact
	1675	4	
Hydrogen	1750	21	Sintered Compact
	1600	4	Sintered Compact
Oxygen	1000	50	Powder
Vacuum	900	210	Powder

*Mallinckrodt U_3O_8 .

**Lindsay Chemical Division Code 529 La_2O_3 .

Following sintering, some of the compacts were crushed, and the calcined powders were oxidized by exposure at 1000°C for 50 hr to tank oxygen flowing at a rate of about 0.5 liter/min. Weights of the powders were determined before and after exposure to assess stoichiometry changes in the powders.

Other portions of calcined powders were vacuum sealed in Vycor capsules in which clean uranium chips had been placed to remove evolved oxygen. The sealed capsules were heated at 900°C for 210 hr. When cool, the powders were isolated from the uranium chips by sealing off capillaries between the samples and the uranium chips. Care was taken not to expose the vacuum-sealed samples to air following the 900°C heat treatment. The uranium constituent in these samples would be reduced essentially to the tetravalent state.

Compacts of lanthana-urania solid solutions which had been sintered at 1675°C for 4 hr in air were subjected to an additional oxidation at high temperatures in order to study the volatility behavior of urania. The metal atom content and stoichiometry of the lanthana-urania compacts were determined prior to heating in a gas-fired furnace at 1675°C for 25, 136, and 310 hr. Combustion gases, slightly rich in oxygen, were passed over the specimens during the heat treatment. The compositions of the specimens investigated ranged from 20 to 80 m/o La_2O_3 . Stoichiometries of the compositions were determined after sintering. Weight, density, and microstructural changes were used as indications of urania loss by vaporization.

Debye-Scherrer patterns of powdered specimens were obtained with copper- $K\alpha$ radiation in a 114.59-mm-diameter camera. Cell dimensions of cubic fluorite solid solutions were determined using the least-squares analytical extrapolation method described by Mueller *et al.*⁽⁹⁾

Polished sections were prepared from sintered specimens by mounting them in Koldmount.* Initial rough grinding was done by grinding with silicon carbide paper. Polishing was done by using, successively, 6- μ , 3- μ , and 1- μ diamond dust. To expose grain boundaries, most of the polished specimens were etched with boiling concentrated phosphoric acid. Specimens which contained free lanthanum oxide were severely attacked by the etch, and these compositions were etched with a solution of 10:1 H_2O_2 : H_2SO_4 .

Chemical analyses were made to determine the U^{+4} , total uranium, and lanthanum contents of selected compositions as affected by environment (oxygen, hydrogen, vacuum, and furnace atmosphere). Stoichiometries of these specimens were determined by calculating the oxidation states of the uranium constituent from the U^{+4} and total uranium analyses, and by assuming that the lanthanum ion was in the trivalent state.

*Vernon-Benshoff Company, Pittsburgh, Pennsylvania.

RESULTS AND DISCUSSION

Extensive fluorite-type solid solution over a considerable portion of the system urania-lanthana was indicated by X-ray analysis. Atmospheric conditions under which the materials were sintered affected the limits of solid solubility.

The base compositions used in this investigation are given in Table III. These compositions were sintered at 1650°C in air for 2 hr. These data are useful in comparing atmospheric effects upon stoichiometry and lattice parameters. Figure 1 and Table IV show the variation in the cubic fluorite-type lattice parameter with composition for the vacuum, hydrogen, and oxidizing heat treatments. Solubility limits for the single-phase solid solutions, as inferred from X-ray data, are shown in Figure 2.

Table III
BASE COMPOSITIONS OF URANIA-LANTHANA SOLID SOLUTIONS
SINTERED AT 1650°C IN AIR FOR 2 HOURS

Specimen No.	Analyzed Composition			Molecular Composition ($U_{\alpha}La_{1-\alpha}O_{\beta}$)		
	Per Cent U	Per Cent La	O/U Ratio	α	$1-\alpha$	β
7U93La	10.24	74.8	2.98	0.074	0.926	1.61
13U87La	17.42	67.4	2.99	0.131	0.869	1.70
20U80La	25.86	58.7	3.00	0.204	0.796	1.81
25U75La	31.82	52.8	2.95	0.260	0.740	1.88
30U70La	35.90	48.5	3.00	0.302	0.698	1.95
35U65La	41.03	43.4	2.93	0.356	0.644	2.01
40U60La	45.33	39.3	2.81	0.402	0.598	2.03
45U55La	50.43	34.4	2.74	0.461	0.539	2.07
50U50La	53.92	30.7	2.77	0.506	0.494	2.14
55U45La	57.93	26.9	2.70	0.557	0.443	2.17
60U40La	61.00	24.0	2.65	0.597	0.403	2.19
65U35La	64.75	20.4	2.60	0.649	0.351	2.22
70U30La	67.76	17.7	2.54	0.691	0.309	2.22
80U20La	74.50	11.1	2.48	0.796	0.204	2.29
90U10La	82.51	6.3	ND	0.891	0.099	- *
95U 5La	84.72	3.2	2.02	0.939	0.061	1.99*

*Hydrogen calcination at 1750°C for 21 hr (UO_2 - La_2O_3 compacts used).

Figure 1.

Lattice Parameters for Urania-Lanthana Solid Solutions

Table IV

X-RAY DATA AND CHEMICAL ANALYSES

Heat Treatment	Metal Atom Composition		Calculated Oxygen-to-Metal Ratio	Cubic Fluorite Lattice Parameter, Å	X-ray Phases Present
	a/o La	a/o U			
Combustion atmosphere at 1650°C for 2 hr	92.6	7.4	1.61	5.6480	La(OH) ₃ +C
	86.9	13.1	1.70	5.6440	La(OH) ₃ +C
	79.6	20.4	1.81	5.6410	C
	74.0	26.0	1.88	5.6077	C
	69.8	30.2	1.95	5.5834	C
	64.4	35.6	2.01	5.5562	C
	59.8	40.2	2.03	5.5396	C
	53.9	46.1	2.07	5.5176	C
	49.4	50.6	2.14	5.5194	C
	44.3	55.7	2.17	5.5007	C
	40.3	59.7	2.19	5.4953	C
	35.1	64.9	2.22	5.4810	C
	30.9	69.1	2.22	5.4753	C
	20.4	79.6	2.29	5.4732	C
Hydrogen atmosphere at 1750°C for 21 hr	92.5	7.5	ND	5.6400	La(OH) ₃ +C
	86.9	13.0	ND	5.6400	La(OH) ₃ +C
	80.0	20.0	ND	5.6430	C+?
	74.9	25.1	1.74	5.6334	C
	69.9	30.1	1.81	5.6136	C
	66.1	33.9	1.87	5.5984	C
	60.0	40.0	ND	5.5879	C
	54.2	45.8	1.94	ND	-
	50.2	49.8	1.95	5.5398	C
	45.4	54.6	1.97	5.5218	C
	40.0	60.0	ND	5.5167	C
	34.9	65.1	1.99	5.5055	C
	29.8	70.2	1.99	5.4963	C
	19.6	80.4	2.00	5.4858	C
	10.0	90.0	ND	5.4767	C
	6.1	93.9	1.99	5.4738	C
	0.0	100.0	2.003	5.4697	-
Vacuum-Uranium chip anneal at 900°C for 210 hr	79.6	20.4	1.71	5.6420	C+?
	69.8	30.2	ND	5.6410	C+?
	64.4	35.6	1.77	5.6204	C
	59.8	40.2	1.79	5.5983	C
	53.9	46.1	ND	5.5808	C
	49.4	50.6	1.83	5.5784	C
	44.3	55.7	1.85	5.5699	C
	40.3	59.7	ND	5.5572	C
	35.1	64.9	ND	5.5408	C
	30.9	69.1	1.92	ND	-
	20.4	79.6	ND	5.5170	C
Oxygen atmosphere at 1000°C for 50 hr	79.6	20.4	1.81	5.6410	C
	69.8	30.2	1.95	5.5840	C
	59.8	40.2	2.03	5.5380	C
	49.4	50.6	2.14	5.5190	C
	40.3	59.7	2.17	5.4950	C
	30.9	69.1	2.22	5.4750	C
	20.4	79.6	2.62	-	Orth. U ₃ O ₈

Figure 2. Cubic Fluorite Solubility Limits for Urania-Lanthana Compositions

Lattice-parameter measurements of solid solutions subjected to the 1650°C oxidizing treatment were in close agreement with the data of Hund and Peetz.⁽⁴⁾ The parameters for single-phase solid solutions increased with increasing lanthana content from 5.4732 Å for 20.4 m/o La₂O₃ to 5.6410 Å for 79.6 m/o La₂O₃. In the compositional range above 87 m/o La₂O₃, characteristic X-ray lines corresponding to La(OH)₃ were evident, as would be expected even in normal humidity. The diffraction patterns obtained from compacts sintered under oxidizing conditions at 1650°C in a gas-fired furnace and those subsequently sintered in oxygen at 1000°C for 50 hr were quite similar. The minor differences noted were probably indicative of slight variations in oxygen content after heat treatment. In the 20 m/o La₂O₃ composition which was subjected to the 1000°C oxidizing atmosphere, no fluorite lines were evident on the diffraction pattern, but characteristic lines of orthorhombic U₃O₈ were observed.

Lattice parameters for the urania-lanthana solid solutions resintered in hydrogen and in vacuum were larger than for those sintered under oxidizing conditions, as may be seen in Figure 1 and Table IV. Parameters of the single-phase solid solutions subjected to hydrogen sintering at 1750°C for 21 hr increased from 5.4738 Å for 61 m/o La₂O₃ to 5.6430 Å for 80.0 m/o La₂O₃. Larger parameters for the solid solutions resintered in vacuum at 900°C for 210 hr were evident. Parameters varied from 5.5170 Å for 20.4 m/o La₂O₃ to 5.6420 Å for 79.6 m/o La₂O₃. Similar cell expansions were noted in other systems containing urania⁽¹⁰⁾ when oxidized compositions were reduced by hydrogen heat treatments. A decrease in solubility limits at higher lanthana contents was evident while the fluorite phase field increased for the high urania compositions under the reducing environments.

The fluorite-type solubility limits determined by polished-section examination of specimens subjected to oxidizing and hydrogen sintering treatments corroborate the limits inferred from X-ray diffraction data. Two-phase microstructures appeared between 75 and 80 m/o La_2O_3 and between 80 and 87 m/o La_2O_3 for the 1600°C hydrogen and 1675°C oxidizing treatments, respectively. Photomicrographs showing the microstructures of three high-lanthana compositions sintered at 1675°C for 4 hr in an oxygen-rich combustion atmosphere are shown in Figure 3. Photomicrographs of the same compositions sintered in hydrogen at 1600°C for 4 hr are shown in Figure 4. Compositions containing 30 to 80 m/o La_2O_3 had single-phase microstructures when sintered at 1675°C in oxidizing environments. The etched 20 m/o La_2O_3 specimen exhibited a microstructure quite different from the 30 m/o La_2O_3 specimen, as is shown in Figure 5. Schaner⁽¹¹⁾ observed a similar behavior for high oxygen-to-uranium atom ratio compositions in the system $\text{UO}_2\text{-U}_4\text{O}_9$. X-ray diffraction showed two fluorite-type patterns for the 20 m/o La_2O_3 specimen, indicating that the observed microstructure was an intimate mixture of MO_{2+x} and M_4O_9 type phase.

The preparation of fully reduced specimens for polished-section examination was precluded because the vacuum-sintered specimens reacted with water and some powdered compositions were pyrophoric in air.

The oxygen-to-metal atom ratios, as deduced from chemical analyses, for the urania-lanthana solid solutions subjected to oxidizing, hydrogen, and vacuum environments are shown in Table IV and Figure 6. In samples subjected to an oxidizing atmosphere at 1650°C for 2 hr, an oxygen-to-metal atom ratio greater than 2.00 existed in the range from 20 to 65 m/o La_2O_3 . The ratio for compositions greater than 65 m/o La_2O_3 was less than the stoichiometric value 2.00 and decreased linearly with increasing lanthana content to a value of 1.50 for pure La_2O_3 . An interesting aspect of these oxygen-deficient compositions is that their uranium contents have been fully oxidized to the U^{+6} state.

Oxygen-to-metal atom ratios of powdered material subjected to an atmosphere of oxygen at 1000°C for 50 hr were calculated from weight change data. With the exception of the 20 m/o La_2O_3 composition, there were no measurable changes from the base powders. A weight increase of 2.17% (based on the urania content) for this composition corresponds to an increase in the oxygen-to-metal atom ratio from 2.28 to 2.62. The transformation of the urania to a U_3O_8 structure, as shown by X-ray diffraction (see Table IV), is evident. In this table the cubic fluorite phase is indicated by C.

7 Mole % UO_2
93 Mole % $\text{LaO}_{1.5}$

Micro 28640

H_2SO_4 Etch

500X

13 Mole % UO_2
87 Mole % $\text{LaO}_{1.5}$

Micro 28641

H_2SO_4 Etch

500X

20 Mole % UO_2
80 Mole % $\text{LaO}_{1.5}$

Micro 31069

H_3PO_4 Etch

500X

Figure 3. Differences in Microstructure for High-lanthana Compositions Sintered at 1675°C for 4 Hours in Combustion Furnace

7 Mole % UO_2
93 Mole % $\text{LaO}_{1.5}$

Micro 29897

H_2SO_4 Etch

500X

13 Mole % UO_2
87 Mole % $\text{LaO}_{1.5}$

Micro 29898

H_2SO_4 Etch

500X

20 Mole % UO_2
80 Mole % $\text{LaO}_{1.5}$

Micro 29899

H_2SO_4 Etch

500X

Figure 4. Differences in Microstructure for High-lanthana Compositions Sintered in Hydrogen at 1600°C for 4 Hours

Figure 5. Differences in Microstructure for High-urania Compositions Sintered at 1675°C for 4 Hours in a Combustion Furnace

Figure 6. Calculated Oxygen-to-metal Atom Ratios for Urania-Lanthana Compositions

In compositions sintered in a hydrogen atmosphere at 1750°C for 21 hr, the oxygen-to-metal atom ratios were lower than those for the base compositions. Specimens containing from 0 to 45 m/o La_2O_3 had oxygen-to-metal ratios close to the stoichiometric value 2.00. Increasing lanthana additions brought about a gradual reduction in the ratio to 1.74 for a 75 m/o La_2O_3 composition. The hydrogen sintering treatment at 1750°C did not appear sufficient to reduce the uranium constituent to the U^{+4} state.

The oxygen-to-metal atom ratios of the vacuum-treated samples (at 900°C for 210 hr) were below those of the hydrogen-sintered compositions. This treatment was not sufficiently severe to reduce the uranium to the U^{+4} state. Experimental difficulties and oxidation problems were encountered in analyzing the specimens, making an estimation of degree of accuracy impossible. Extrapolation of lattice parameters, however, indicated that the oxidation state was lower than the reported results.

X-ray diffraction data and chemical analyses indicated that useful information could be obtained by investigating the dependence of lattice parameters on the stoichiometry of a composition of, initially, constant

metal atom content. A 50 m/o La_2O_3 composition was heated in vacuum, in hydrogen, and in an oxidizing atmosphere. The stoichiometry of the composition varied from 1.78 to 2.16, as shown in Table V and in Figure 7.

Table V

LATTICE PARAMETERS AND OXYGEN-TO-METAL (O/M) RATIOS
FOR $\text{U}_{0.5}\text{La}_{0.5}\text{O}_{1.75+x}$ COMPOSITIONS

Temp (°C)	Time (hr)	Remarks	Lattice Parameter (Å)	O/M Ratio
900	210	Vacuum in presence of uranium chips	5.5784	1.78*
1900	6	Vacuum approximately 10^{-7} mm	5.5664	1.83
1750	21	Hydrogen	5.5398	1.92*
		Hydrogen; specimen oxidized during 6 months of storage	5.5305	1.95
1450	155	Sintered compact annealed in air	5.5179	2.06
1675	4	Sintered compact	5.5187	2.09
1650	2	Calcined powder	5.5194	2.14
1000	50	Calcined powder in 1 atm oxygen	5.5200	2.16

*No chemical analysis determination; O/M ratio inferred from lattice-parameter measurements.

Figure 7

Effect of Stoichiometry on the Lattice Parameter for a $\text{U}_{0.5}\text{La}_{0.5}\text{O}_{1.75+x}$ Solid Solution

The lattice parameters of these treated compositions indicate a diminution of cell dimension with increasing oxygen content. The plot of these values in Figure 7 shows a definite break in the curve near stoichiometric $\text{MO}_{2.0}$. The parameters for substoichiometric solid solutions decreased linearly with increasing oxygen-to-metal atom ratio at a slope near -0.30 , while the variation in ratio for the hyperstoichiometric compositions was negligible. The break at 2.00 suggests that two different mechanisms govern the accommodation of oxygen in the cubic fluorite-type structure of these solid solutions.

Oxidized urania exhibits an appreciable vapor pressure under oxidizing conditions at temperatures in excess of 1200°C .⁽¹⁾ To study the suppression of this volatilization by combining the urania in a solid solution, compacts of urania and lanthana were sintered at 1675°C for 4 hr in

Figure 8. Oxygen-to-metal Atom Ratios for Urania-Lanthana Compositions Sintered at 1675°C for 4 Hours in Air

an oxidizing atmosphere and were subsequently heat treated in an oxygen-rich atmosphere for 25, 136, or 310 hr. The oxygen-to-metal atom ratios for the compositions sintered at 1675°C for 4 hr are given in Figure 8. The microstructures of the compositions, which varied from 20 to 80 m/o La_2O_3 , are shown in Figure 9.

The effect of sintering time upon the microstructures of these sintered compacts is shown in Figures 10, 11, 12, 13, and 14. Figure 10 shows the effect upon grain growth and microstructure in a 20 m/o UO_2 -80 m/o La_2O_3 composition. Densification and grain growth can be noted for 20 m/o UO_2 -

80 m/o La_2O_3 (see Figure 10); for 30 m/o UO_2 -70 m/o La_2O_3 (see Figure 11); and for 40 m/o UO_2 -60 m/o La_2O_3 (see Figure 12). Only slight microstructural changes were noted in the higher urania compositions, as shown in Figure 13 for 60 m/o UO_2 -40 m/o La_2O_3 and particularly in Figure 14 for 80 m/o UO_2 -20 m/o La_2O_3 .

Table VI shows the compositions studied, the density of the sintered compacts, and the weight loss encountered in the compacts upon extended heat treatment. The effect of composition on the weight loss of exposed surface area is shown in Figure 15. Samples containing more than 60 m/o La_2O_3 had low weight losses, and their loss rates were essentially constant. Microstructure examination, as shown in Figure 16,

Figure 9. Microstructures of Urania-Lanthana Specimens Sintered in a Combustion Furnace at 1675°C for 4 Hours

Exposure Time

As Sintered

25 Hours

136 Hours

310 Hours

Micro 31039

250X

Micro 31046

250X

Micro 29900

250X

Micro 31055

250X

Etchant: 50 Parts H_3PO_4 (85%) 50 Parts H_2O , Boiling

Figure 10. The Effect of Time on Microstructure of 20 Mole % UO_2 80 Mole % $\text{LaO}_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C

Exposure Time

As Sintered

25 Hours

136 Hours

310 Hours

Micro 31040

250X

Micro 31047

250X

Micro 31052

250X

Micro 31056

250X

Etchant: 50 Parts H_3PO_4 (85%) 5 Parts H_2O , BoilingFigure 11. The Effect of Time on Microstructure of 30 Mole % UO_2 70 Mole % $\text{LaO}_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C

Exposure Time

As Sintered

25 Hours

136 Hours

310 Hours

Micro 31041

250X Micro 31048

250X Micro 29902

250X Micro 31057

Etchant: 50 Parts H_3PO_4 (80%), 50 Parts H_2O , Boiling

Figure 12. The Effect of Time on Microstructure of 40 Mole % UO_2 60 Mole % $\text{LaO}_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C

Exposure Time

As Sintered

25 Hours

136 Hours

310 Hours

Micro 31043

100X

Micro 31049

100X

Micro 29904

100X

Micro 31058

100X

Etchant: Boiling Concentrated H_3PO_4 Figure 13. The Effect of Time on Microstructure of 60 Mole % UO_2 40 Mole % $\text{LaO}_{1.5}$ Specimens Subjected to Combustion Gases at 1675°C

Exposure Time

As Sintered

25 Hours

136 Hours

310 Hours

Micro 31045

100X Micro 31050

100X Micro 29906

100X Micro 31059

100X

Etchant: Boiling Concentrated H_3PO_4

Figure 14. The Effect of Time on Microstructure of 80 Mole % UO_2 20 Mole % $LaO_{1.5}$ Specimens Subjected to Combustion Gases at $1675^{\circ}C$

Table VI

DATA FOR URANIA-LANTHANA SPECIMENS SUBJECTED TO COMBUSTION GASES AT 1675°C

Specimen No.	Exposure Time, hr	Per Cent Theoretical Density	Per Cent Open Porosity	Weight Loss/Exposed Surface Area (mg/cm ²)
20U80La	0	84.7	12.5	-
	25	92.3	0.1	+0.3*
	136	94.1	0.1	1.3
	310	94.9	0.1	7.9
30U70La	0	90.5	0.6	-
	25	94.9	0.1	1.5
	136	96.3	0.1	4.8
	310	96.0	0.2	11.8
40U60La	0	88.6	0.9	-
	25	92.6	0.1	3.4
	136	93.8	0.9	14.4
	310	92.6	2.3	36.6
50U50La	0	91.6	0.0	-
	25	92.3	0.8	10.9
	136	90.3	2.4	29.4
	310	88.8	4.8	72.2
60U40La	0	91.4	0.0	-
	25	89.7	1.8	38.3
	136	78.5	13.2	158.0
	310	81.8	10.7	150.0
80U20La	0	94.2	0.1	-
	25	92.5	1.8	49.5
	136	74.4	18.7	373.0
	310	70.5	24.0	395.0

*Weight Gain Noted

Figure 15.

Effect of Composition on Weight Loss for Urania-Lanthana Solid Solutions Subjected to Combustion Gases at 1675°C

Mole % UO_2
Mole % $\text{LaO}_{1.5}$

20

80

30

70

40

60

60

40

80

20

Micro 31060

250X

Micro 31061

250X

Micro 31062

250X

Micro 31063

100X

Micro 31064

100X

Etchants: Boiling H_3PO_4 - H_2O

Figure 16. Surface Porosities for Urania-Lanthana Specimens Subjected to Combustion Gases at 1675°C for 310 Hours

indicated that grain growth and densification had occurred and that the specimen surfaces were relatively inert to attack by the furnace gases. Specimens within this range had oxygen-to-metal atom ratios below the stoichiometric $\text{MO}_{2.00}$ and were the most stable with regard to volatility behavior.

High-urania specimens, containing from 20 to 50 m/o La_2O_3 , had much higher weight losses, and their exposed surfaces appeared to be attacked by furnace gases. Microstructure examination indicated that the excessive weight losses were accompanied by increases in open porosity near the exposed surfaces (see Figure 16). These specimens had high-porosity penetrations as compared with the high-lanthana compositions. Attack on high-urania specimens appeared to occur by urania vaporization along grain boundaries. A decrease in volatility rate was noted after long exposure and may have been caused by vapor saturation within the porosity channels. The oxygen-to-metal atom ratio of these compositions was greater than 2.10. Specimens with compositions in the range from 55 to 60 m/o La_2O_3 had oxygen-to-metal ratios between 2.07 and 2.01. These compacts had intermediate surface attack (see Figure 16).

The low volatility of compositions containing more than 60 m/o La_2O_3 cannot be explained adequately by the dilution effects of lanthanum for uranium substitution. This would result in a linear relation between urania loss and lanthana composition. The stoichiometry differences between volatile and nonvolatile compositions in changing from an oxygen-deficient to an oxygen-excess structure appears to be a significant factor in the volatility behavior of these solid solutions.

SUMMARY

Fluorite-type solid solubility existed over a considerable portion of the system urania-lanthana. Experimental environments affected the solubility limits and lattice parameters of the compositions. Cubic, fluorite-type, solubility extended from 30 to 80 m/o La_2O_3 for combustion-atmosphere sintering; from 0 to 75 m/o La_2O_3 for hydrogen-atmosphere sintering; and from 0 to 75 m/o La_2O_3 for vacuum heat treatment. The variation in lattice parameter for samples that were initially of identical cation content suggests that stoichiometry differences have occurred for specimens subjected to various environments.

Deviations from stoichiometric $(\text{U,Lu})\text{O}_{2.00}$ were noted for compositions subjected to different heat treatments. The oxygen content of compositions containing less than 45 m/o La_2O_3 were close to stoichiometry.

Densification and grain growth occurred in urania-lanthana samples exposed for extended periods of time to combustion gases at 1675°C. This

change was more pronounced in compositions containing below 60 m/o La_2O_3 . Urania vaporization was noted at these extended heating times, but the extent of vaporization was less at the higher lanthana contents.

BIBLIOGRAPHY

1. R. J. Ackermann, R. J. Thorn, C. Alexander, and M. Tetenbaum, Free Energies of Formation of Gaseous Uranium, Molybdenum, and Tungsten Trioxides, J. Phys. Chem., 64, 350-55 (1960).
2. A. S. Bain and J. A. L. Robertson, Effects of O:U Ratio on the Irradiation Behavior of Uranium Oxide, J. Nuclear Materials, 1(1) 109-10 (1959).
3. J. S. Anderson, D. N. Edgington, L. E. J. Roberts, and E. Wait, Oxides of Uranium: IV, System $\text{UO}_2\text{-ThO}_2\text{-O}$, J. Chem. Soc., 1954, 3324-31.
4. F. Hund and U. Peetz, Investigation of the Systems La_2O_3 , Nd_2O_3 , Sm_2O_3 , Yb_2O_3 , Sc_2O_3 , with U_3O_8 , Z. anorg. u. allgem. chem., 271, 6-16 (1952).
5. E. D. Lynch, J. H. Handwerk, and C. L. Hoenig, Oxidation Studies of Urania-Thoria Solid Solutions, J. Amer. Ceram. Soc., 43(10), 520-24 (1960).
6. D. Kolar, J. H. Handwerk, and R. J. Beals, Investigations in the System Urania-Neodymia, ANL-6631 (Dec 1962).
7. W. B. Wilson, Stabilization of UO_2 by Valence Compensation, BMI-1318 (Feb 1959).
8. W. A. Lambertson and M. H. Mueller, Uranium Oxide Phase Equilibrium Systems: III $\text{UO}_2\text{-ZrO}_2$, J. Amer. Ceram. Soc., 36(11), 365-68 (1953).
9. a. M. H. Mueller, L. Heaton, and K. T. Miller, Determination of Lattice Parameters with the Aid of a Computer, Acta. Cryst., 13, 828-29 (1960).
b. M. H. Mueller and LeRoy Heaton, Determination of Lattice Parameters with the Aid of a Computer, ANL-6176 (1961).
10. W. Rudorff and G. Valet, Cerium Uranium Blue and Solid Solutions in the System $\text{CeO}_2\text{-UO}_2\text{-U}_3\text{O}_8$, Z. anorg. u. allgem. chem., 271 (5-6), 257-77 (1953).
11. B. E. Schaner, Metallographic Determination of the $\text{UO}_2\text{-U}_4\text{O}_9$ Phase Diagram, J. Nuclear Materials, 2(2), 110-20 (1960).