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STABILIZATION OF UO_2 BY VALENCE COMPENSATION

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Wendell B. Wilson

Uranium dioxide, when heated in air, will transform to U_3O_8 . The U_3O_8 which is formed exhibits appreciable vapor pressure at temperatures in excess of 1200 C. The need for a stable high-temperature nuclear fuel requires prevention of the U_3O_8 transformation as well as a lowering of the vapor pressure. A method by which this may be accomplished involves compensation of the valence change of uranium, as it undergoes oxidation. This is accomplished by massive addition of other metal oxides.

Solid-state studies of the uranium-lanthanum-oxygen system were conducted in the present investigation to elicit more detailed understanding of the processes involved.

The oxidation and vaporization characteristics of uranium dioxide were compared directly to solid solutions of uranium dioxide containing from 30 to 60 w/o of La_2O_3 . These solid solutions, which have the fluorite structure, were formed by reacting UO_2 and La_2O_3 in vacuo. When these materials were oxidized the fluorite structure was retained with, however, reduced lattice parameters. These were shown to be equivalent to reacting U_3O_8 with La_2O_3 . The volatility of the resulting solid solutions was found to vary with the amount of additive. The composition exhibiting the lowest vapor pressure was further related to a stoichiometry between the cation and anion content.

The usual approach in "alloying" to improve oxidation resistance is to retard the rate of oxidation. The present approach differs in that the alloying material is added to stabilize the structure and results in rapid oxidation. However, since no phase change is involved marked improvement in stabilization is obtained. An attempt to generalize the concepts developed for application to other oxide systems is made.

INTRODUCTION

The use of uranium dioxide as a nuclear fuel suffers from several inherent limitations. If the fuel is operated under an oxidizing environment as a normal condition or as a result of failure, it will undergo oxidation from UO_2 to U_3O_8 . In a composite fuel element the cladding intended to protect the UO_2 may fail, and the volume expansion of the UO_2 transforming to U_3O_8 may disrupt the element. In addition, if the reactor is required to operate in excess of 1375 C, the U_3O_8 will vaporize with a resultant loss of fuel.⁽¹⁾ The desirability of developing a dimensionally and structurally stable material which does not suffer from these limitations is obvious.

Published research⁽²⁾ indicates that the vapor pressure of uranium oxide varies as a function of the crystal structure. Thus, the UO_2 fluorite structure, which is quite refractory in nonoxidizing atmospheres, might well prove to be refractory in an oxidizing atmosphere, if somehow the structure could be prevented from transforming to U_3O_8 . Since the uranium ion, in the course of oxidation, goes from the +4 to the +6 valence state, the problem resolves itself into modifying the material so that this valence change can occur without allowing a change in crystal structure.

(1) References at end of report.

The exact behavior of uranium oxide in air at temperatures of the order of 1200 to 1400 C has been masked by simultaneous oxygen dissociation and volatility of the solid.⁽²⁾ This has resulted in some uncertainty in the interpretation of the behavior of oxides under these conditions. For instance, Lang, et al.,⁽³⁾ interpreted anomalous weight-change data near these temperatures as "...indicative of dissociation of higher uranium oxides to form a UO_2 -like structure even in the presence of oxygen." As another alternative to dissociation Lang suggested the possibility that the high-temperature UO_2 formed might undergo vapor transfer as a hydrate, similar to BeO . The possibility that the higher uranium oxide was volatile does not appear to have been considered. Since U_3O_8 is a volatile oxide, it appeared desirable to extend the investigation of uranium oxide containing various oxide additives to higher temperatures. This was done to determine if improved "stabilization" could be achieved with respect to volatility and phase as well as dimensional stability.

In previous research ceramic "binary" systems (actually ternaries) were formed by reaction of various metal oxides with UO_2 and U_3O_8 . These preliminary results strongly suggested that the prepared materials behaved, in general, in a predictable manner similar to the Hume-Rothery "rules" for metals. That is, where the relative valence effect, ion size, and other factors were favorable, solid solutions would tend to form and where they were badly mismatched solubility was limited and compound formation was probable. In some instances, such as the BeO - UO_2 system, the additive ion size and valence were sufficiently dissimilar as to apparently preclude any type of reaction at normal pressure.

After these solid solutions had been prepared, they were subjected to air oxidation at temperatures producing measurable volatility. The first such system to be examined was the UO_2 - ThO_2 system. The materials were initially reacted by firing in hydrogen to form a solid solution. The lattice parameter of the solid solution was observed essentially to follow Vegard's⁽⁴⁾ law. However, after prolonged air firing it was found that the lattice parameter increased slowly toward the value for pure ThO_2 . Chemical analysis subsequently confirmed that uranium, probably as U_3O_8 , was evaporating from the structure preferentially.

Continuing work disclosed, however, that the UO_2 - La_2O_3 solid solution, after air firing, indicated only a slight change in lattice parameter with continued oxidation. The difference detected between the UO_2 - La_2O_3 and the UO_2 - ThO_2 systems strongly suggested that a tetravalent additive was considerably less beneficial than a trivalent additive. Investigation with other oxide additives in solid solutions indicated that the physical properties were markedly affected by the additive valence and amount. The present investigation was performed to obtain more detailed knowledge of the factors involved.

Valence Compensation

The attention drawn to the valence behavior of both the uranium and the additive served to point out that in some fashion a material of less than +4 valence appeared capable of compensating for the +4 to +6 valence change that occurs with oxidation of UO_2 . The zone theory of solids has shown⁽⁵⁾ that the valence electrons in all solids, by virtue of the "tunnel effect", are free to move or migrate, and are not to be completely identified with individual atoms. Such conclusion, in a sense, suggests that in a solid solution, an "averaging" of valence electrons in a crystal might well occur. Thus, as the uranium ion undergoes oxidation from the +4 to the +6 valence state, sufficient +2 or

+3 material, added to the solid, might adjust the average valence back to the +4 state, nominally required by the fluorite structure. The fact that a sesquioxide could stabilize the UO_2 fluorite structure was apparently first realized by Lambertson(6) who, however, felt that the amount of additive oxide was too large to be of practical significance. However, the volatility of uranium oxide drastically alters this condition.

The UO_2 - La_2O_3 system was selected as a model system to investigate the "average valence" concept. The structure of La_2O_3 is hexagonal rare-earth "A" type. However, it is possible to retain the cubic rare-earth "C" type structure under certain conditions.(7) Sesquioxides will in general, fall into the rare-earth "A" or "C" type in conformance with the radius ratio of metal to oxide ion. Thus when $r(\text{R})/r(\text{O}) \geq 0.87$ the hexagonal "A" structure is favored and when the ratio is between 0.53 and 0.87 the cubic fluoritelike "C" structure is formed.(7,8) For this reason Sc_2O_3 and Y_2O_3 are of the rare-earth "C" type, due to their small ion size and La_2O_3 is "C" type only at lower temperatures. Small additions of uranium to La_2O_3 , however, stabilize the "C" structure(7); the smaller uranium ion apparently averaging with the lanthanum to produce a radius ratio of <0.87 . Thus minor additions of UO_2 to La_2O_3 tend to form a fluoritelike rare-earth "C" type structure, similar to UO_2 with an average cation valence of nominally +3.

EXPERIMENTAL WORK

The experimental work involved in "stabilization" requires a combined investigation in several areas. These included chemical composition, metallographic and structural studies, and physical properties. It is, of course, essential that structural studies by diffraction be conducted to determine the phases involved. When the initial solid solutions are formed and air oxidized, some components may be volatilized preferentially and others adsorbed. For instance, in a UO_2 - ThO_2 body the uranium apparently is lost as uranium oxide even while the entire body picks up oxygen. Thus, the total weight, in "short-time oxidation" may remain nearly constant, yet a radical change in both composition and crystal structure is possible. For this reason weight-change data alone are useless. Thus, in order to achieve a full understanding of the processes involved, it is essential that each area be investigated. Electrical measurements were determined for certain of the materials investigated here to provide a better understanding of the additive role in stabilization.

Material Preparation

Ceramic bodies of UO_2 with varying amounts of La_2O_3 , ThO_2 , CaO , and Sc_2O_3 were prepared. In general, the amounts to be added were weighed to conform to the "valence-compensation" criteria as follows:

where R' is assumed to go to the +6 valence state (with oxidation) and sufficient R'' is added to adjust the right side of the equation to the +4 valence state. In both of the above reactions it is apparent that the additive oxide deviates from RO₂ type (there is too little oxygen for each R'' metal cation) with the result that the reacted product is a nonstoichiometric defect solid solution which accordingly must be oxidized to stoichiometry.

The preparation of the materials may also be approached in an entirely different fashion similar to the manner in which Hund et al. (7,9-13) prepared their "anomalous" solid solutions.* Here the uranium may be added in the oxidized state as U₃O₈. Thus, the orthorhombic structure of U₃O₈ may combine with either the hexagonal or cubic rare-earth sesquioxides to form a fluorite structure. From this, it may be seen that it is possible to produce a cubic fluorite-structure solid solution even though neither component has the fluorite structure. These reactions differ from those of Reactions (1) and (2) as follows:

In Reactions (3) and (4), it may be seen that the fluorite-structure solid solutions are more nearly stoichiometric than in (1) and (2). In the above reactions, (1) and (2) refer to reacting UO₂ with the additive oxides, and (3) and (4) refer to reacting U₃O₈ (approximated as UO₃) in place of UO₂. The resultant solid solutions represent the reduced and oxidized condition, respectively, for the fluorite structure so formed.

An important point occurs in considering the two possible alternatives to producing the solid solutions. That is, it is entirely possible to have unfavorable solubility conditions toward formation of a solid solution with one oxide, and favorable conditions with the other. This follows as a result of the variation of the size of the uranium ion, which is 1.05 Å for the +4 valence state and reportedly 0.81 Å for the +6 state. (7) Thus, Sc₂O₃, with a scandium ion size of 0.81 Å reacts with U₃O₈ to form a solid solution but does not react with U⁺⁴ whose ion size is 1.05 Å. The lattice parameter of the resulting fluorite solid solution of U₃O₈ plus Sc₂O₃ was found to be 5.13 Å as opposed to 5.23 Å found by Hund et al. (15) The Hund value appears to be a probable misprint in view of their data.

Fabrication

The desirability of obtaining electrical measurements on the samples necessitated a preparation which was as pure as possible compatible with the high sintering temperatures. Although a variety of sample-preparation techniques was investigated, only the final technique used will be described. The oxide additive powders were vacuum dried to remove adsorbed water prior to mixing with UO₂. The powders were weighed in an argon-filled dry box and compacted hydrostatically at 100,000 psi using a binder of 1 w/o beeswax in CCl₄. The compacts were placed on high-fired UO₂ blocks and

*See also Reference (14) for a discussion of the CeO₂-UO₂ to U₃O₈ mixed crystals.

sintered in vacuum using a graphite susceptor and induction heating. The sintering temperatures were usually 1750 C for a period of 2 to 4 hr. Following the initial reaction, the compacts were recrushed and reprocessed to produce bodies of higher density which were free of cracks and voids. Bodies were prepared approximating the compositions in Table 1.

TABLE 1. NOMINAL COMPOSITIONS
OF EXPERIMENTAL
OXIDE SAMPLES
AS MIXED

Composition, w/o	
UO ₂	Additive
95	5 CaO
90	10 CaO
70	30 CaO
55	45 Sc ₂ O ₃
60	40 La ₂ O ₃
50	50 La ₂ O ₃
40	60 La ₂ O ₃
50	50 ThO ₂

The purity of the UO₂-50 w/o La₂O₃ additive, prepared as given above, indicated 275 ppm metallic impurity with titanium, at 100 ppm, being the largest contaminant. Other elements were present at 50 ppm or less. The carbon content was 0.01 w/o and originated, in all probability, from the carbon vapor of the diffusion pump and the graphite susceptor. Attempts to lower the carbon and other impurities were not successful.

Oxidation Studies

The oxidation characteristics of the fabricated materials relative to that of UO₂ were evaluated by weight-change analysis. This was accomplished in two ways, by continuous microbalance weighing of small powder samples and by periodic analytical-balance weighing of more massive bodies and powders. The microbalance studies provided a "dynamic" method of following the oxidation behavior while the long-time oxidation studies with larger amounts of material permitted postoxidation chemical analysis to determine which element, if any, vaporized preferentially. These studies were intended to indicate if a material did or did not volatilize, and, since this did not require a detailed knowledge of particle size, it was not determined.

The microbalance studies clearly indicated that all materials oxidized immediately when exposed to air at 1550 C. The initial air oxidation was followed by a subsequent weight loss of all materials tested except that of UO₂ with 60 w/o La₂O₃ additive, which remained constant after oxidation. The microbalance data at the lower, 1375 C, temperature indicated that the UO₂, which had oxidized to U₃O₈, did not lose weight. This would indicate that the adequate sublimation temperature of U₃O₈ had apparently not quite been reached. Table 2 summarizes the data obtained by use of the microbalance apparatus on solid solutions of La₂O₃. Data for a UO₂-50 w/o ThO₂ body are included.

TABLE 2. SUMMARY OF REACTIONS OF UO_2 AND $\text{UO}_2\text{-La}_2\text{O}_3$ MIXTURES WITH AIR AT HIGH TEMPERATURES BY MICROBALANCE TECHNIQUES

Composition, w/o		Temperature, C	Relative Initial Weight Gain, per cent		Rate of Weight Change ^(a) After Initial Gain, g per min
UO_2	La_2O_3		Total Sample	UO_2 Content	
100	--	1375	3.75	3.75 ^(b)	0
68	32	1375	2.52	3.70	0
100	--	1550	3.83	3.83	-6.3
60	40	1550	2.25	3.78	-2.4
50	50	1550	1.64	3.28	-1.2
40	60	1550	1.43	3.60	0
50	50 ThO_2	1550	0	0	-3.5

(a) For 2 hr.

(b) Theoretical weight gain for conversion of UO_2 to U_3O_8 is 3.95 per cent.

Data obtained by use of the microbalance were substantiated by longer time oxidation testing using larger amounts of material, which permitted chemical analysis. In these tests, UO_2 and solid solutions of variable composition were tested by firing in air and determining the weight change. Some samples were chemically analyzed for uranium/additive cation ratio before and after the tests to determine if preferential loss of either cation occurred. These extended oxidation tests were performed to evaluate the comparative performance of the trivalent solid solutions with those of tetravalent additives, i. e., $\text{UO}_2\text{-La}_2\text{O}_3$ versus $\text{UO}_2\text{-ThO}_2$.

Samples were fired both as powders and as ceramic bodies. The bodies were used to evaluate weight change and tendency toward cracking or pulverizing. The powders permitted more rapid and complete oxidation than the bodies, since structural studies indicated that the "stabilized" materials "passivate" themselves by forming a fully oxidized layer on the surface which retards interior oxidation. The air-oxidation experiments were performed using materials fabricated by various techniques, resulting from attempts to fabricate bodies of high purity and uniform density for electrical measurements. The variations in fabrication produced minor variations in oxidation as well as other physical characteristics dependent on factors such as density and porosity. In addition, the air flow rate and the access of the air to the samples tested produced variations in weight change, particularly at the lower, 1375 C, temperature. For these reasons, a direct comparison of one sample group to another in the following oxidation tests is inadmissible, and the experiments are described individually.

Each of five air-oxidation experiments of larger amounts of material will be described. These range from air-fired UO_2 alone to a direct comparison of $\text{UO}_2\text{-60 w/o La}_2\text{O}_3$ and $\text{UO}_2\text{-50 w/o ThO}_2$.

The first test was a direct comparison of bodies of UO_2 , $\text{UO}_2\text{-10 w/o CaO}$, and $\text{UO}_2\text{-50 w/o ThO}_2$. It should be noted that none of these materials was "stabilized" and they had been prepared by a different technique than previously described. They were fabricated by a single hydrogen sintering at 1760 C of bars compacted at 18,000 psi with 1/4 oz camphor in 100 cm^3 alcohol as a binder. The sintering was accomplished by placing the bars on the edges of tilted rectangular UO_2 blocks. The UO_2 blocks were

placed on molybdenum sheet which in turn rested on a BeO slab. The molybdenum and BeO were found to be impurities which possibly affected the oxidation characteristics as well as electrical measurements. The weight-loss data obtained by air oxidation of these materials are given in Figure 1. The per cent weight loss is expressed as the per cent of the original UO_2 content in each body. The samples were fired at 1375 C at linear air flow rate (forced) of 20 in. per min. It may be seen that the bodies gained weight initially in direct relationship to the amount of uranium they contained. This was subsequently followed by a decrease in weight of all the materials.

In the second experiment UO_2 , UO_2 -45 w/o Sc_2O_3 , and UO_2 -50 w/o La_2O_3 were placed in Alundum boats and air oxidized at 1375 C for 3 hr in a Globar type furnace. These materials were prepared by the double-sintering technique previously described. The weight-change data of these samples are contained in Table 3. Structural studies indicated that, although the UO_2 had transformed to U_3O_8 , as can be seen in Table 3, it had not increased to theoretical weight. This may be attributed to its rapidly achieving theoretical weight, as indicated by the microbalance studies, and subsequently subliming. The sublimed U_3O_8 condensed as single crystals of alpha U_3O_8 as reported in Reference (1). The UO_2 body was decomposed to powder by oxidation.

TABLE 3. WEIGHT GAINED BY UO_2 AND UO_2 -RARE-EARTH OXIDE COMPACTS DURING HEATING FOR 3 HR IN AIR AT 1375 C

Material	Total Weight Gain, per cent	Weight Gain Based on UO_2 Content, per cent
UO_2	2.69	2.69(a)
UO_2 -45 w/o Sc_2O_3	1.92	3.49
UO_2 -50 w/o La_2O_3	1.82	3.64

(a) Theoretical weight gain for complete conversion of UO_2 to U_3O_8 is 3.95 per cent.

The UO_2 -45 w/o Sc_2O_3 body, as previously described, did not form a solid solution. After air firing, however, it was found that the material did form a solid solution. This body was expanded by the reaction but still retained its original shape. For this reason, air-sintered U_3O_8 - Sc_2O_3 is of potential interest as a stabilized material. The UO_2 -50 w/o La_2O_3 remained dimensionally unchanged by the oxidation. Both of the solid solutions were found to achieve more nearly the theoretical weight change corresponding to its proportion of UO_2 oxidizing to U_3O_8 than did UO_2 alone.

In the third oxidation experiment, bodies of UO_2 with additions of 40, 50, and 60 w/o La_2O_3 and 50 w/o ThO_2 were heated in air for 4, 6, 8, and 10 hr at 1375 C. The data for these experiments are given in Table 4. Comparison of these data with the microbalance data indicated the same general characteristics of rapid initial oxidation. However, a slight decrease in the weight of all specimens fired was noted in addition to the usual decomposition of the UO_2 - ThO_2 body. The microbalance data indicated that the sample with the 60 w/o La_2O_3 addition did not suffer a weight loss at 1550 C, whereas the data in Table 4 indicate a small weight decrease at 1375 C. This apparent anomaly is probably due to impurities introduced by different fabrication techniques. (The samples indicating the weight decrease at 1375 C contained in excess of 1 w/o tantalum, picked up by use of a tantalum instead of a graphite susceptor in the vacuum sintering in an attempt to produce carbon-free material.)

FIGURE 1. WEIGHT-LOSS DATA OBTAINED FOR UO_2 , UO_2 -50 w/o ThO_2 , AND UO_2 -10 w/o CaO IN FIRST OXIDATION EXPERIMENT

TABLE 4. SUMMARY OF REACTIONS OF $\text{UO}_2\text{-La}_2\text{O}_3$ AND $\text{UO}_2\text{-ThO}_2$ MASSIVE SINTERED BODIES WITH AIR AT 1375 C

Composition	Relative Weight Gain ^(a) at Indicated Time, per cent							
	4 Hr		6 Hr		8 Hr		10 Hr	
	Total Sample	UO_2 Content	Total Sample	UO_2 Content	Total Sample	UO_2 Content	Total Sample	UO_2 Content
$\text{UO}_2\text{-50 w/o La}_2\text{O}_3$	+1.18	+2.36	-0.29	-0.58	-0.28	-0.56	-0.23	-0.46
$\text{UO}_2\text{-50 w/o ThO}_2$	+0.72	+1.44	-0.56	-1.12	-0.65	-1.30	-0.87	-1.74
$\text{UO}_2\text{-60 w/o La}_2\text{O}_3$	+1.67	+4.19	-0.04	-0.10	+0.02	+0.05	-0.13	-0.33
$\text{UO}_2\text{-40 w/o La}_2\text{O}_3$	+0.96	+1.60	-0.06	-0.10	-0.01	-0.02	-0.19	-0.32
UO_2	+0.37				+2.40			

(a) Theoretical weight gain for conversion of UO_2 to U_3O_8 is 3.95 w/o.

A plus (+) sign indicates weight gain; a minus (-) sign indicates a weight loss.

The anomaly between results of the second and third oxidation test was resolved by a fourth oxidation test at 1375 C for a period in excess of 100 hr. Compositions of UO_2 -60 w/o La_2O_3 and UO_2 -50 w/o ThO_2 were compared directly with each other. The UO_2 -50 w/o ThO_2 body fractured into small grains with oxidation, and small pieces were expelled from the boat. The UO_2 -60 w/o La_2O_3 body remained intact, changing only in color. It is estimated that the UO_2 -50 w/o ThO_2 body lost about 9 per cent by weight. The UO_2 -60 w/o La_2O_3 gained 2.5 per cent by weight, which is roughly equivalent to its conversion to stoichiometry by oxidation.

Chemical analysis indicated that there was preferential loss of uranium from the UO_2 -50 w/o ThO_2 while the uranium content in the UO_2 -60 w/o La_2O_3 remained unchanged. Table 5 shows the comparative analysis. The lattice parameters of these materials showed the usual rapid decrease with oxidation. The values obtained are plotted in Figure 2 and Figure 3 in accord with analyzed composition. The UO_2 -50 w/o ThO_2 indicated complete oxidation while the UO_2 -60 w/o La_2O_3 was somewhat "passivated" as will be shown.

TABLE 5. DIRECT COMPARISON OF UO_2 CONTAINING La_2O_3 AND ThO_2 ADDITIVES BEFORE AND AFTER 107 HR OF AIR OXIDATION AT 1375 C(a)

Mixed Composition	Weight Change, per cent	UO ₂ Content, w/o	
		Before	After
UO_2 -60 w/o La_2O_3	+2.50	58	57
UO_2 -50 w/o ThO_2	-9.0	47	41

(a) Lattice-parameter changes are given in Figures 2 and 3.

The results of a fifth oxidation experiment are given in Table 6. Here the temperature has been increased to 1650 C, where pronounced volatility occurs. The table shows that UO_2 had lost nearly 6 per cent weight, in spite of the weight increase, due to oxidation, after 1 hr at 1650 C. At 20 hr 62 per cent of the material had evaporated. Other stabilized materials are included for comparison. The UO_2 -30 w/o La_2O_3 -5 w/o CaO represents preliminary work to reduce the 60 w/o La_2O_3 needed for stabilization. The UO_2 -30 La_2O_3 -50 ThO_2 is a preliminary sample potentially suitable for an improved breeder fuel. These tests indicate promise from such materials.

Structural Studies

Insight into the behavior of these materials undergoing oxidation may be accomplished through examination of the accompanying structural changes by diffraction analysis. Figure 2 represents the lattice parameters of the UO_2 - La_2O_3 system, both as fabricated and following air oxidation. The X-ray results of Hund and Peetz(7) for $\text{U}_3\text{O}_8 + \text{La}_2\text{O}_3$ also are included for direct comparison, since the latter represents the "fully oxidized" condition of the solid solutions. The latter data are converted from kX units to Angstroms and all values are plotted in accordance with the actual chemical analysis of the materials rather than the as-mixed analysis, which is slightly different.

FIGURE 3. LATTICE PARAMETERS OF UO_2-ThO_2 AFTER HUND, NIESSEN, AND TRZEBIATOWSKI

FIGURE 2. SOLID SOLUTION REGION $\text{UO}_2\text{-U}_3\text{O}_8\text{-La}_2\text{O}_3$ SYSTEM

Parameter versus analyzed composition except where indicated.

TABLE 6. WEIGHT CHANGES RESULTING FROM HEATING UO_2 AND STABILIZED UO_2 IN ATMOSPHERIC AIR AT 1650 C

Material	Time at 1650 C, hr	Total Weight Gain ^(a) , per cent	Average Weight Gain, per cent per hr of heating
UO_2	1	-5.82	-5.82
UO_2 -60 w/o La_2O_3 ^(b)	1	0.19	0.19
UO_2 -30 w/o La_2O_3 -5 w/o CaO	1	0.98	0.98
UO_2 -30 w/o La_2O_3 -50 w/o ThO_2	1	0.75	0.75
UO_2	20	-62.7	-3.14
UO_2 -30 w/o La_2O_3 -5 w/o CaO	20	1.71	0.09
UO_2 -30 w/o La_2O_3 -50 w/o ThO_2	20	6.28	0.31

(a) Minus sign indicates weight loss.

(b) Previously heated at 1375 C for 107 hr in air.

The lattice-parameter studies show that the $\text{UO}_2\text{-La}_2\text{O}_3$ solid solutions follow Vegard's law from 0 to more than 60 w/o with the lattice parameter increasing linearly with increasing La_2O_3 composition. Values were not obtained above 60 w/o since these were somewhat beyond the solid-solution range of current interest in valence studies. (Previous work had indicated that a second phase occurs in significant amounts, which is substantiated by Hund and Peetz.)

The lower line of Figure 2 is a plot of the Hund and Peetz lattice-parameter data for the $\text{U}_3\text{O}_8\text{-La}_2\text{O}_3$ system. It may be seen that with less than 33 w/o La_2O_3 , free U_3O_8 was detected, and above 70 w/o La_2O_3 , free La_2O_3 was detected. Between these two values, however, the solid-solution region of fluorite structure exists. Thus a solid-solution fluorite type structure extends from UO_2 to $\text{UO}_2\text{-60 w/o La}_2\text{O}_3$ and from $\text{U}_3\text{O}_8\text{-33 to 70 w/o La}_2\text{O}_3$.

The intermediate values between the UO_2 and the U_3O_8 parameter data of Figure 2 were obtained by air oxidation of the $\text{UO}_2\text{-La}_2\text{O}_3$ bodies and powders. In each instance, the lattice parameter decreased to an intermediate value which was, however, considerably larger than the $\text{U}_3\text{O}_8\text{-La}_2\text{O}_3$ counterpart. This has been shown to arise from a "passivating" surface on the bodies which impedes oxidation beneath it. The outermost surface of each air-oxidized body exhibited a lattice parameter which is considerably smaller than the interior indicating that the surface was more fully oxidized than the interior. Further oxidation of the $\text{UO}_2\text{-La}_2\text{O}_3$ is inhibited apparently by formation of an outer surface which at the optimum composition is virtually stoichiometric. This stoichiometric composition reduces diffusion, thereby retarding oxidation.

Tetravalent Additive

Previous work had shown that, of the refractory tetravalent oxides, TiO_2 , ZrO_2 , and ThO_2 , only ThO_2 formed extensive solid solutions with UO_2 . The $\text{ZrO}_2\text{-UO}_2$ system had been shown by Lambertson and Mueller(16) and more recently by Wolten(17) to contain a miscibility gap below 2000 C. The reaction of TiO_2 and UO_2 resulted in formation of complex crystal structures, apparently since the Ti^{+4} ion size is unfavorable to form a solid solution with UO_2 . For this reason ThO_2 was selected as the tetravalent additive to UO_2 . However, only preliminary results are available here confirming previous results and are included only to show the difference in behavior between tetravalent and trivalent additives.

The equivalent of the "reduced" and "oxidized" states of the $\text{UO}_2\text{-ThO}_2$ system and $\text{U}_3\text{O}_8\text{-ThO}_2$ system have been reported.(10,18-20) The lattice parameters of compositions of $\text{UO}_2\text{-ThO}_2$ were found to follow Vegard's law. Hund and Niessen(10), however, found that in the $\text{U}_3\text{O}_8\text{-ThO}_2$ system (representing the fully oxidized state of the $\text{UO}_2\text{-ThO}_2$ system) a "break" was indicated near 57 mole per cent of U_3O_8 . Figure 3 shows a direct comparison of these data, plotted in Angstroms. It will be noted that, as before in Figure 2, Vegard's law may be used for depicting the lattice parameter of $\text{UO}_2\text{-ThO}_2$. Further, upon oxidation, the U^{+4} ion goes to the smaller U^{+6} ion, thereby reducing the lattice parameter. The oxidized state, however, does not follow Vegard's law over the complete compositional range, since free U_3O_8 is formed at high uranium content.

Structural studies were conducted on the UO_2 -50 w/o ThO_2 solid solutions after oxidation for 107 hr. In general, after solid solutions were formed, air oxidation was observed to produce two phases with distinct lattice parameters. The larger of the lattice parameters, which is obviously due to a ThO_2 -rich phase, was observed to remain more nearly constant, while the smaller (UO_2 -rich) lattice parameter decreased with oxidation initially and then subsequently increased to become essentially a solid solution again after 107 hr at 1375 C in air. Table 7 shows the lattice-parameter behavior observed.

TABLE 7. LATTICE-PARAMETER CHANGE OF UO_2 - ThO_2 MATERIAL AS A FUNCTION OF AIR OXIDATION AT 1375 C

X-Ray No.	Lattice Parameter, A	Time at 1375 C, hr
53	5.545	0
49	5.53 and 5.48	10
56	5.515 and 5.54	42
60	5.52	107

If these observations do not arise from inhomogeneity in the starting materials, then the "peculiar" behavior of the UO_2 - ThO_2 solid solution upon oxidation may be related in some way to the fracturing which is characteristically observed when these materials are oxidized. Although ThO_2 provides certain benefits with respect to UO_2 oxidation, it appears that a small amount of phase change occurring at the grain boundaries might account for the fracturing. Further, such phase change, the product of oxidation, would possibly allow the more volatile oxide to evaporate.

Electrical Studies

Electrical studies of the UO_2 with mixed oxides were initiated for correlation to the oxidation behavior. Electrical characteristics of UO_2 plus oxygen have been previously studied⁽²¹⁾. Impurities resulting from high sintering temperature, together with variations in fabrication techniques, densities, and other factors, presented obstacles to a detailed interpretation of the electrical characteristics. As indicated, the present electrical studies deal with UO_2 plus additions (or effectively the "reduced" state of the solid solutions). The "oxidized" equivalent for some oxide additions may be interpreted by reference to the work of Hund, et al., especially Reference (9).

The role of the additive oxide was studied by determination of the magnitude and type of electrical conductivity of specimens containing Ca^{+2} , Th^{+4} , and La^{+3} additions. Preliminary work relative to the temperature dependence of the conductivity and thermoelectric power also was initiated to determine the effect of valence and ion size of the additive on the properties of UO_2 . Details of this initial work will not, however, be described here.

Table 8 lists values obtained for room-temperature resistivity and type of conductivity. The table shows that metal ions of different size and valence markedly affect

TABLE 8. ELECTRICAL CHARACTERISTICS OF MATERIALS

Sample	Composition, w/o	Resistivity, ohm-cm	Conductivity Type
8	100 UO_2	3.84×10^2	p
9	95 UO_2 -5 CaO	1.3×10^2	p
10	90 UO_2 -10 CaO	8.25×10	p
12	50 UO_2 -50 ThO_2	2.07×10^4	p
25(a)	70 UO_2 -30 La_2O_3	1.2×10^5	p
16(a)	66 UO_2 -33 La_2O_3	2.5×10^3	p
37	60 UO_2 -40 La_2O_3	5×10^4	
15(a)	58 UO_2 -42 La_2O_3	1.1×10^5	p
26(a)	53 UO_2 -47 La_2O_3	7.7×10^6	
28	50 UO_2 -50 La_2O_3	(b)	
13	45 UO_2 -55 La_2O_3	1.4×10^4	p
36(a)	43 UO_2 -57 La_2O_3	(b)	
24(a)	41.5 UO_2 -58.5 La_2O_3	2.5×10^7	n
31A	50 UO_2 -50 La_2O_3	4.8×10^2 (c)	p

(a) Analyzed compositions.

(b) Too high to measure.

(c) Heated in air at 2500 F, 3 hr.

the electronic properties of the solid. The addition of increasing amounts of CaO causes an increase in the p -type conductivity of the solid. The opposite effect is observed with La_2O_3 , where increasing the additive decreases p -type conductivity. In fact, La_2O_3 solid solutions were observed to become n -type between 55 and 60 w/o La_2O_3 . This value is nearly identical with the value given by Hund et al. (7) as the point at which the cation and anion partial lattices attain stoichiometry.

Values of the energy necessary to activate a charge carrier were obtained from the slope of the extrinsic portion of the curve of conductivity versus temperature from -78 to 500 C. A value of 0.36 ev was obtained for the UO_2 with CaO additions. This value is essentially the same as that for UO_2 containing excess oxygen and suggests that the Ca^{+2} ion is substitutional for uranium in accord with diffraction results. Similar measurements with the UO_2 - La_2O_3 materials indicated that the activation energy to free a charge carrier is independent of La_2O_3 concentration (over the range tested) and was 0.60 ev. This, however, was found to drop to 0.40 ev when the materials were exposed to air at room temperature where slight oxidation occurred. It should be mentioned that the sintered compacts partially oxidize spontaneously upon exposure to air and in one instance (UO_2 -40 w/o La_2O_3) the material was pyrophoric. This behavior was also found by other investigators for UO_2 with divalent and trivalent additive solid solutions. (22, 23)

The behavior of the UO_2 -CaO solid solutions appears to be "normal" from an intuitive standpoint. Since Ca^{+2} can supply only two of the required four valence electrons to the defect fluorite structure, an electron-deficient material results which has increasing p -type conductivity with increasing CaO content. Although La^{+3} would be expected to introduce different energy levels than Ca^{+2} , from the same qualitative reasoning, it would be expected that increasing La_2O_3 content should cause an increase in conductivity. In this case, observed behavior is exactly opposite to that expected, since increasing amounts of La_2O_3 decrease the p -type conductivity. At 58 w/o La_2O_3 the material has an immeasurably small conductivity and at somewhat higher La_2O_3 content, n -type behavior was observed. Stoichiometric UO_2 , as an insulator, would be expected to have nonoverlapping filled and empty bands. As La_2O_3 is added, p -type conductivity is obtained. At present it appears that the conductivity increases to a maximum and returns to a typical insulator at 58 w/o La_2O_3 , beyond which there is a phase change. Thus, the material apparently goes from an insulator to a defect semiconductor to a defect insulator in a solid-solution region. A detailed explanation of this unique behavior must await further study of the solid solutions.

PRINCIPLES OF STABILIZATION OF THE UO_2 FLUORITE STRUCTURE

A qualitative explanation of "stabilization" may be advanced by means of the band or zone theory of solids. The use of this concept appears attractive for several reasons. Experimentally, the major criteria for selection of an additive are atom size and valence. The zone theory provides a means of qualitatively considering the effects of both. The extreme complexity of application of the theory to all but relatively simple materials precludes quantitative application. However, it appears possible to adopt the electron/atom ratio concept for the stoichiometric oxide which occurs upon

oxidation, as will be discussed. Although the phase behavior may be described by other explanations, such as the valence "oscillation" concept of Hund, et al.,⁽⁹⁾ the band concept as utilized by Hume-Rothery⁽²⁴⁾ and especially by Jones for alloys⁽²⁵⁾ appears more suitable.

The application of the zone concept to these materials was undertaken to provide a nonempirical basis for additions. However, it should be emphasized that the concept as used here is highly qualitative. Significant differences exist between the conditions in a metal and an insulator, which, while apparently not changing the qualitative nature of the concept, would appear to limit a direct correspondence. Thus, the condition of maximum stability of a metal is obtained when the Fermi surface just touches the edges of the zone. Since the density of states decreases rapidly beyond this point the number of electrons with maximum energy is not readily accommodated and a new phase becomes stable. This condition cannot exactly prevail in an insulator since the zone is already assumed to be filled. Further the energy contours are assumed nearly spherical for free electrons in metals and considerable departure from this must occur for insulators.

Hume-Rothery has shown for alloys that when the ion size, relative valence, and other factors are favorable solid solutions tend to form. When these conditions for solubility are not met, alloys tend to be insoluble or to form compounds. This similarity between the mixed oxides and alloys in this respect suggests that application of the Hume-Rothery approach used for metals may be permissible for oxides. The valence-compensation criterion previously discussed is simply the equivalent of the Hume-Rothery electron/atom ratio concept for alloys. The concept in itself is merely a method of both qualitatively and semiquantitatively applying the zone approximation to instances when detailed calculations are not possible.

The validity of applying the zone theory to crystalline materials other than metals is frequently questioned, in spite of the fact that it provides the explanation of the difference between metals and insulators. This apparently stems from the fact that the theory is basically derived from the Bloch one-electron approximation (analogous to a monovalent metal) where it is assumed to be a "free electron". Insulators are usually considered more ionic in nature than metals and for this reason it is customary to assume that the electron plays a more localized role in the vicinity of the atom. Seitz⁽²⁶⁾ and others have discussed the problem at length, but for the present purpose it may be concluded that the theory may be used for insulators — with reservation. The reservation is, of course, that the electron may actually be localized near the atom and will not be as free to move throughout the crystal as in an ideal metal. Thus, although all valence electrons are free to move throughout a crystal some may move with more facility than others, depending upon the degree of mobility of electrons in the valence level itself.* For the present purposes, it is experimentally true that the valence electrons are sufficiently nonlocalized to allow an "averaging" in the solid.

*Mott⁽²⁷⁾ has recently reopened the issue by showing that there are classes of insulators which he believes to contain unfilled bands but which do not conduct because of the localized wave function of the electron around the ion. He cites NiO as an example of such a material. Whether this is true in fact is a controversial subject.

Studies of the uranium-oxygen phase diagram have indicated that the fluorite structure of UO_2 is stable from a composition of UO_2 to $\text{UO}_{2.33}$. Strictly speaking this is not quite true at lower temperatures(28-30) but is certainly true at the temperatures of present consideration. Oxygen diffuses into the UO_2 and forms a defect structure.* This excess oxygen in uranium dioxide may be considered to alter the zone structure in that it changes the lattice parameter of the solid in addition to affecting changes in the valence structure. These changes can continue until the structure becomes strained and unstable and begins to transform to tetragonal. The strain which produces the transformation may result, from similar reasoning, to that advanced by Jones for the copper-zinc system, which serves as the basis of the zone theory of alloy phases. From his work(25) it is shown that, when other factors (such as atom size, valence, etc.) are insignificant, an alloy will adopt a crystal structure which will allow it the lowest possible Fermi energy, and this is accomplished when the interplanar spacing for Bragg reflection is very near the smallest wavelength of the electrons moving perpendicular to that spacing. Thus, there is associated with each phase a limited range of stability over which it is possible for it to exist and when the Fermi surface either overfills or underfills the zone, strain results which eventually necessitates a transformation. Thus, as oxygen is added to UO_2 the lattice parameter is decreased, resulting in an expansion in "k" space.** Further, the effect of oxygen is to cause p-type conductivity which means that both valence and ion size move in a direction to decrease the number of electrons in the zone volume. At a nominal composition of $\text{UO}_{2.33}$ or $\text{U}^{4.66}$ the strain is apparently sufficient to produce a transformation.

The effect of adding La_2O_3 to UO_2 is twofold. It increases the lattice parameter which results in a decrease in the zone volume. Concomitantly it does not have as many valence electrons to contribute as does the uranium. Thus, while the zone volume is reduced, the number of valence electrons in the zone volume also is decreased at the same time and the solid solutions are stable in the reduced state. Oxidation of the reduced UO_{2-60} w/o La_2O_3 decreases the lattice parameter toward that of the U_3O_8 - La_2O_3 composition of Hund, et al., in Figure 2. This decrease results in an expansion of the zone, which again increases the p-type conductivity in accord with the experimental results. Here, however, the situation is quite different from that of UO_2 above. The zone structure is apparently filled in the reduced state, yet the solid solution has only one-third of its total cation content which can change valence due to oxidation. Even if all of the uranium goes from +4 to +6 valence state, the resulting change is not sufficient to produce a change in phase. At a composition near U_3O_8 -58 mole per cent La_2O_3 (63 w/o), Hund found a stoichiometric composition (intact cation and anion partial lattices). It is this stoichiometric composition, when produced on the surface, that impedes further oxidation.

It is of interest to further examine this concept by consideration of other systems. For the sesquioxides the picture is essentially the same as for La_2O_3 and their behavior may be derived from the comparison of the UO_2 - R_2O_3 solid solutions to those of Hund for U_3O_8 - R_2O_3 . A very excellent example of this is a comparison of the work of Ferguson and Fogg(22) with that of Hund, et al.(9) for the yttria-urania system. The divalent additives are interesting from another standpoint. The relative valence effect is sufficiently dissimilar that solubility is limited. If both valence and ion size are different, solubility is negligible.*** For this reason, the zone picture is more limited since factors other than Fermi energy are significant.

*The exact nature of the defect structure and its temperature dependence is not clear.

**A nonmathematical description of zone theory, suitable for present use, is contained in Reference (5).

***See Table 9 for a comparison of ionic radii of some cations.

TABLE 9. IONIC RADII^(a)

Ion	Radius, A
U ⁺⁴	1.05
U ⁺⁶	0.81
Th ⁺⁴ (b)	1.02
Zr ⁺⁴ (c)	0.80
Ti ⁺⁴ (c)	0.64
La ⁺³ (b)	1.22
Y ⁺³ (b, c)	0.93
Sc ⁺³ (c)	0.81
Al ⁺³	0.50
Ca ⁺² (b)	0.99
Mg ⁺²	0.65
Be ⁺²	0.31

(a) Table does not consider relative valence effect on solubility. The "anomalous" solid solutions of Hund, et al., occur when U₃O₈ reacts with an unfavorable ion size (i. e., lanthanum) to form an extensive solid solution.

(b) Ion size favorable for solid solution with UO₂.

(c) Ion size favorable for solid solution with U₃O₈.

U⁺⁴ radius $\pm$ 15 per cent = 0.89 A to 1.22 A

U⁺⁶ radius $\pm$ 15 per cent = 0.68 A to 0.93 A.

The Ca⁺² ion is the same size as U⁺⁴ and solubility is large⁽³¹⁾, being 40 mole per cent at 1950 C. As the Ca⁺² ion is added to UO₂ the lattice parameter is decreased slightly. Since Ca⁺² has insufficient valence electrons for the fluorite structure, an increase in the p-type conductivity is found for increasing CaO. Both lattice parameter and, especially, valence contribute to emptying the zone and the solubility is more limited than for the trivalent additive.

The addition of MgO is especially interesting from this standpoint. The Mg⁺² ion radius is given as 0.78 A. This is too small and the valence too divergent from U⁺⁴ (ion radius of uranium is 1.05 A) to react with UO₂ to any extent.⁽³⁾ However, this is not the case for U⁺⁶ where the ion radius is reduced to 0.81 A. When MgO-UO₂ is oxidized, the solubility increases markedly to 26 mole per cent, forming a fluorite structure.

For the tetravalent additives, ZrO₂ and ThO₂, similar characteristics are found. As ThO₂ is added to UO₂, complete solubility is found, since the relative valence and ion size are quite similar. The electrical characteristics of ThO₂ additives to UO₂ were reported by Gruen⁽³¹⁾ and shown to be related to oxygen excess in accord with the amount of uranium in the solid solution. The ThO₂ itself expands the lattice parameter, which decreases the zone volume. Since oxidation is in the reverse direction to this, marked improvement in phase stability during oxidation is obtained for the ThO₂ additive bodies. The same picture of valence compensation would suggest that bodies of high ThO₂ content, such as UO₂-75 w/o ThO₂ should be relatively stable even from the volatility standpoint.

ZrO₂ additions to UO₂ lower the lattice parameter, since the radius of Zr⁴⁺ is 0.80 Å. This results in an expansion of the zone and in the middle of the phase diagram(15,16) a solid immiscibility region results between the cubic fluorite structure and a tetragonal structure. Although these materials have not been investigated in the present work, speculation would suggest that a small addition of Th⁴⁺ or La³⁺ would expand the solid, resulting in elimination of the immiscibility region. The oxidation behavior of the UO₂-ZrO₂ system, although unreported, should be of decided interest. The similarity of ion size between Zr⁴⁺ and U⁶⁺ should allow some solubility.

Electron/Atom Ratio

The preceding discussion showed in a qualitative way the fact that a solid-solution phase region varies in breadth as a function of additive valence and, to a lesser extent, additive ion size. This rather elementary picture was derived principally as a means of deducing what additive ion size and valence should be optimum for prevention of transformation resulting from oxidation. The quantitative derivation of phase limits by use of the detailed zone picture is, at present, prohibitively difficult. To circumvent this type of difficulty, Hume-Rothery introduced the electron/atom ratio concept for metals. The concept involves substitution of the number of valence electrons per atom as an approximation for the total number of electrons in the unit cell. This is possible since the number of electrons in the unit cell is a simple multiple of the number of electrons per atom. This is, of course, strictly true only if the structure is stoichiometric. By use of the electron/atom ratio concept an arbitrary limit of phase existence may be defined for nonmetallic solids as well as metals.

The UO₂ fluorite structure can exist from UO₂ to nominally UO_{2.33} corresponding to a uranium (cation) valence of U⁴⁺ to U^{4.66}. Assuming that this is the phase field limit, expressed in electrons per atom, then by use of the valence compensation criteria previously discussed, it is possible to derive equivalent values for the electron/atom ratios of the solid solutions.

The concept neglects consideration of the effects of lattice parameter and is strictly valid for only one concentration of the solid solution, namely, that corresponding to:

where UO₃ is written as an approximation to U₃O₈ and the resulting composition corresponds to the nearly stoichiometric solid solution of Hund. It should be mentioned that valence compensation, as presented here, essentially ignores the relative amount of ionic versus covalent character of the oxides in accord with Pauling's criteria.⁽³²⁾ This would amount to a correction requiring slightly larger amounts of stabilizing oxide to be added, and would arise principally due to the differences in electronegativity of additive cation versus uranium. It will be recalled that the general picture of valence compensation requires a sufficient amount of a lower valence material to be added to offset the U⁴⁺ to U⁶⁺ transition resulting from oxidation. In general, for phase stability it is required that an amount be added to bring the solid solution back into the range where the average valence of uranium plus additive is between +4.0 and +4.66. Further, it is experimentally evident that the most satisfactory composition of a solid solution from the standpoint of vaporization is the tetravalent state.

The ideal composition for stoichiometry according to Hund is U_3O_8 -58 mole per cent (63 w/o) La_2O_3 , with the fluorite phase field existing from 30 mole per cent La_2O_3 to 65 mole per cent. Consideration of Reaction (5) above indicates that, at equimolar ratios of UO_2 and La_2O_3 , for each uranium ion going from +4 to +6 there are two +3 lanthanum ions available providing compensation. Thus, the valence criterion suggests compensation at 50 mole per cent and Hund reports an ideal lattice at 58 mole per cent. The difference of 8 mole per cent may possibly be attributed to the fact that the electronegativities are not exactly the same for the uranium and lanthanum ions.

According to Hund, 30 mole per cent La_2O_3 is the lowest amount which will prevent the formation of U_3O_8 . This fact may be directly compared to $\text{UO}_{2.33}$ which is the highest oxidized state allowed by the fluorite structure for urania before phase change. The average valence of a solid solution may be obtained by use of the following relation.

$$\bar{R} = \frac{\sum_{A_1}^{A_n} \text{Mole Per Cent } A_i \times \text{Valence } R_{A_i} \times \text{Atoms per Molecule } A_i}{\sum_{A_1}^{A_n} \text{Mole Per Cent } A_i \times \text{Atoms per Molecule } A_i},$$

where A_i refers to the compound such as UO_2 or La_2O_3 and R_{A_i} is the cation of the compound. For U_3O_8 with 30 mole per cent La_2O_3 the resulting average valence is found to be +4.6 which is in agreement with the $\text{UO}_{2.33}$ electron/atom ratio. U_3O_8 results when the average valence exceeds +4.66. Reference to the data of Hund shows that the other sesquioxides exhibit similar behavior.

The UO_2 - ThO_2 system, on the basis of Hund's data, retards formation of U_3O_8 up to a composition of 57 mole per cent U_3O_8 . The average valence of a solid solution of this composition is +5.14 which is much too high for the fluorite structure. The reasons for this are quite uncertain. If the UO_2 - ThO_2 solid solutions behave similarly to UO_2 and to the trivalent additives, it would appear that a composition of UO_2 -66 w/o ThO_2 would have, on oxidation, the maximum average valence of +4.66. It will be recalled that the present studies indicated volatility of uranium oxide in UO_2 -50 w/o ThO_2 bodies, suggesting that the stable fluorite structure had been exceeded at this composition.

The divalent additives of MgO and CaO also require equimolar amounts for valence compensation to occur and, as will be recalled, the solubility does not permit this for either additive. To determine if a UO_2 - CaO solid solution corresponding to $\text{UO}_{2.33}$ occurs, an average valence might in effect be calculated. In general, it would require about 1/3 mole of divalent additive. CaO is nearly able to achieve this solubility in the reduced state and bodies fabricated with CaO as additive are somewhat stable although they have a high rate of oxidation. MgO , on the other hand, is not sufficiently soluble in U_3O_8 for significant compensation to occur.

SUMMARY

Uranium dioxide-base fuels which may be oxidized or reduced without dimensional or structural changes have been developed. Basically, the fuel is formed by reacting UO_2 with other oxides to form a solid solution. It will be recalled that UO_2 upon oxidation transforms to U_3O_8 . By utilizing concepts obtained from the theory of phase changes in metals, the amount of the additive oxide necessary to prevent the disruption transformation may be estimated. The process involves the compensation of the valence change which occurs when U^{+4} is oxidized to U^{+6} . A sufficient quantity of certain trivalent or divalent materials is added in solid solution to compensate for the uranium valence change. The resulting solid solution, when formed, has the UO_2 fluorite structure, which can exist over a relatively large range of defect composition. Upon oxidation the material tends to become stoichiometric, resulting in a "passivating" influence occurring at the surface.

The UO_2 - La_2O_3 system was chosen as a model system for investigation to obtain an understanding of the fundamentals involved. La_2O_3 , along with a number of other sesquioxides, when added to UO_2 forms a solid solution. However, since La_2O_3 has insufficient valence for the fluorite structure, the resulting solid solutions are defect structures having anion vacancies. This defect solid solution exists up to about 60 mole per cent La_2O_3 . When these materials are oxidized, it is found that the lattice parameters are changed but the structure remains the same. The terminal point of oxidation is equivalent to mixing U_3O_8 and La_2O_3 together, which also form solid solutions. Passivation of the UO_2 - La_2O_3 material occurs when the UO_2 and La_2O_3 are mixed in correct proportions to produce upon oxidation a stoichiometric cation-to-anion ratio. The lack of defects in the resulting structure impedes further oxidation by diffusion.

The region over which the fluorite structure exists is found to be affected both by the valence of the additive and the size of the additive ion, as well as the oxygen content. The rate of oxidation is determined by the degree of imperfection in the solid solutions, with some materials spontaneously oxidizing in air.

The material, in reduced state, may allow improved fission-gas retention in the vacancies of the defect solid solution. For composite fuel elements in gas-cooled reactors or other instances where a failure would allow oxidation of fuel the stability of the material should be of benefit. Application, to other oxide systems, of the concepts utilized in the development of the fuel appears possible.

FUTURE WORK

The present investigation was directed toward obtaining a more detailed understanding of the concepts used to "stabilize" the UO_2 fluorite structure. This was done under the premise that a basic understanding of the processes involved would permit direct application to other oxide systems and also serve as a basis for alloy development itself. Several immediate areas for research investigation suggest themselves as a result.

The amount of material required to effect stabilization of UO_2 is quite large, and would represent an appreciable portion of core space. By use of the concepts developed here, it appears feasible to reduce the 60 mole per cent of sesquioxide necessary to effect stabilization. The tendency of $\text{UO}_2\text{-ThO}_2$ bodies to fracture and to lose uranium upon oxidation may be overcome through substitution of stabilized uranium oxide as additive for ThO_2 . This material would represent a possible improved fuel. Work toward these two possibilities has already been initiated and the preliminary results appear satisfactory.

One of the more significant areas is the direct application of the concepts used here to other volatile oxides such as MoO_3 and WO_3 or for that matter to oxide systems where stabilization of a certain oxide phase would present significant advantages in prevention of transformation. If this should prove successful, a basis for nonempirical alloy development of the refractory metals would be possible.

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REFERENCES

- (1) Wilson, W. B., "U₃O₈ Single Crystals", APEX-202 (June, 1955). Secret.
- (2) Katz, J. J., and Rabinowitch, F., The Chemistry of Uranium, McGraw-Hill Book Company, Inc., New York (1951), pp 253, 263.
- (3) Lang, S. M., Knudsen, F. P., Fillmore, C. L., and Roth, R. S., "High Temperature Reactions of Uranium Dioxide With Various Metal Oxides", Natl. Bur. Standards Cir. No. 568, p 4 (1956).
- (4) Vegard, L., Z. Physik, 5, 17 (1921).
- (5) Cottrell, A. H., Theoretical Structural Metallurgy, Edward Arnold, Ltd., London (1955), p 66.
- (6) Lambertson, W. A., and Mueller, M. H., "Uranium Oxide Phase Equilibrium Systems, V, $\text{UO}_2\text{-Nd}_2\text{O}_3$ ", ANL-5312 (September 14, 1954).

- (7) Hund, Von F., and Peetz, V., "Untersuchungen der Systeme La_2O_3 , Nd_2O_3 , Sm_2O_3 , Yb_2O_3 , Sc_2O_3 mit U_3O_8 ", Z. anorg. u. allgem. Chem., 271, 6 (1952-1953).
- (8) Wyckoff, R. W. G., Crystal Structures, Interscience Publishers, Inc., New York (1951).
- (9) Hund, Von F., Peetz, U., and Kottenhan, G., "Das Systeme Yttriumoxyd-Uranoxyd", Z. anorg. u. allgem. Chem., 278, 184 (1954-1955).
- (10) Hund, Von F., and Niessen, G., "Anomale Mischkristalle in System Thoriumoxyd-Uranoxyd", Z. Elektrochem., 56, 972 (1952).
- (11) Hund, Von F., Wagner, R., and Peetz, U., "Anomale Mischkristalle im System Cerdioxid-Uranoxyd", Z. Elektrochem., 56, 61 (1952).
- (12) Hund, Von F., and Peetz, U., "Die Fluoritphasen im System Praseodymoxyd-Uranoxyd", Z. Elektrochem., 56, 223 (1952).
- (13) Hund, Von F., and Peetz, U., "Die Fluoritphasen im System U_3O_8 - Er_2O_3 ", Z. anorg. u. allgem. Chem., 267, 189 (1952).
- (14) Rudorff, Von W., and Valet, G., "Über das Ceruranblau und Mischkristalle im System $\text{CeO}_2 \cdot \text{UO}_2 \cdot \text{U}_3\text{O}_8$ ", Z. anorg. u. allgem. Chem., 271, 257 (1952-1953).
- (15) Reference (7), p 14.
- (16) Lambertson, W. A., and Mueller, M. H., "Uranium Oxide Equilibrium Systems, III, $\text{UO}_2 \cdot \text{ZrO}_2$ ", J. Am. Ceram. Soc., 36, 365 (1953).
- (17) Wolten, G. M., Presented at 133rd Meeting American Chemical Society, San Francisco, April 13-18, 1958.
- (18) Slowinsky, F., and Elliott, N., "Lattice Constants and Magnetic Susceptibilities of Solid Solutions of Uranium and Thorium Dioxide", Acta Cryst., 5, 768 (1952).
- (19) Lambertson, W. A., Mueller, M. H., and Gunzel, F. H., Jr., "Uranium Oxide Equilibrium Systems, IV, $\text{UO}_2 \cdot \text{ThO}_2$ ", J. Am. Ceram. Soc., 36, 397 (1953).
- (20) Trzebiatowski, W., and Selwood, P. W., "Magnetic Susceptibilities of Urania Thoria Solid Solutions", J. Am. Chem. Soc., 72, 4504 (1950).
- (21) Willardson, R. K., Moody, J. W., and Goering, H. L., "The Electrical Properties of Uranium Oxides", J. Inor. & Nuclear Chem., 6, 19 (1958).
- (22) Ferguson, I. F., and Fogg, P. G. T., "The Oxides of Uranium, Part VIII, The System Uranium Dioxide-Yttria", J. Chem. Soc., 3679-81 (1957).
- (23) Reference (3), p 11.
- (24) Hume-Rothery, W., "Atomic Theory for Students of Metallurgy", J. Inst. Metals (London) (1955).

- (25) Jones, H., "Applications of the Bloch Theory to the Study of Alloys and the Properties of Bismuth", Proc. Roy. Soc. (London), 396 (1934).
- (26) Seitz, F., Modern Theory of Solids, McGraw-Hill Book Co., Inc., New York (1940).
- (27) Mott, N. F., Recent Advances in the Electron Theory of Metals, Progress in Metal Physics, Interscience Publishers, Inc., New York (1952), Vol. 3, p 76.
- (28) Reference (3), p 11.
- (29) Vaughan, D. A., Bridge, J. R., and Schwartz, C. M., "Comparison of Active and Inactive Uranium Dioxide-Oxygen Systems", BMI-1241 (December 10, 1957).
- (30) Willardson, R. K., Moody, J. W., and Goering, H. L., "The Electrical Properties of Uranium Oxides", BMI-1134 (September 25, 1956).
- (31) Gruen, D. M., J. Am. Chem. Soc., 76 (1954).
- (32) Pauling, L., The Nature of the Chemical Bond, Cornell University Press, Ithaca (1940), p 69.

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