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STABILIZATION OF TUNGSTEN - URANIUM DIOXIDE COMPOSITES UNDER THERMAL CYCLING CONDITIONS

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by Richard E. Gluyas and Michael A. Gedwill

Lewis Research Center
Cleveland, Ohio

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STABILIZATION OF TUNGSTEN - URANIUM DIOXIDE COMPOSITES UNDER THERMAL CYCLING CONDITIONS (U)

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SUMMARY

X67-50022

Uranium losses during thermal cycling of tungsten - uranium dioxide composites to 2500° C in flowing purified hydrogen for specimens initially containing 35 volume percent uranium dioxide were reduced by the use of thorium dioxide, calcium oxide, or yttrium oxide as additives in solid solution with the uranium dioxide. The effectiveness of the additives decreased in the order yttrium oxide, calcium oxide, and thorium dioxide. Stabilization of uranium dioxide by calcium oxide or yttrium oxide can be explained in part on the basis of the introduction of oxygen vacancies into the fluorite lattice and the associated lowered partial molar free energy of oxygen. The difference in the effectiveness of calcium oxide and yttrium oxide is discussed, and a possible explanation of the observed behavior is proposed. Of the concentrations of yttrium oxide tested (i. e., 2. 5, 5, and 10 mole percent), 10 mole percent of yttrium oxide was the most effective in preventing loss of uranium from composities.

Author

INTRODUCTION

Previous work on materials for a tungsten, water-moderated, nuclear rocket reactor (ref. 1) showed that tungsten - uranium dioxide ($W-UO_2$) composites rapidly lose fuel at high temperature (e. g., 2500° C) in a flowing, dry, hydrogen atmosphere (ref. 2). It was demonstrated that volatilization losses due to continuous heating can be controlled by surface-cladding the composites with tungsten; however, losses due to thermal cycling could not be satisfactorily prevented in this way (i. e., <1 percent fuel loss after 25 cycles to 2500° C, refs. 2 and 3). Such thermal cycling losses were reduced in $W-UO_2$ composites containing 20 volume percent UO_2 by addition of thorium dioxide (ThO_2) to the tungsten matrix, by use of fine UO_2 particles (~1 μ in. diam), and, more effectively, by

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solid solution additions of calcium oxide (CaO), zirconium dioxide (ZrO_2), or ThO_2 to the UO_2 (ref. 4).

Since the latter approach appeared to be especially promising, the work was continued in this study with special emphasis on the use of stabilizing additives in W-UO_2 cermets containing the maximum loading of UO_2 (35 volume percent) anticipated in the thermal reactor concept. The additives CaO, yttrium oxide (Y_2O_3), and ThO_2 were included for study in order to determine the effect of the valence of the cation and of the additive concentration on the fuel loss during thermal cycling to 2500° C in hydrogen. The effect of complete as opposed to partial surface cladding with tungsten also was measured.

To minimize the effect of uncontrolled variables in fabrication and testing, the principles of randomization and replication were incorporated in the major part of the experiments described in this report.

EXPERIMENTAL

Approach

Two factors affecting weight loss from specimens of UO_2 particles dispersed in a tungsten matrix during thermal cycling to 2500° C were studied in the first part of the experimental work, namely, the kind and the concentration of stabilizing additives in solid solution with UO_2.

The specimens contained 35 volume percent (i.e., 23 weight percent) of UO_2 dispersed in tungsten, had 1.4- by 1.0- by 0.018-inch (3.5- by 2.5- by 0.045-cm) dimensions, and were clad on the major faces with about a 0.0018-inch (0.0046-cm) thick layer of tungsten. The edges of the specimens used in this part of the work were not clad. The compositions studied included UO_2 with no additive and UO_2 with nominal concentrations of 2.5, 5, and 10 mole percent of CaO, Y_2O_3, or ThO_2 in solid solution. Calcium oxide was also studied at the 15 mole percent level. Tungsten was used as the matrix material.

To increase confidence in the results, the various solid solutions, plates, or specimens were processed in a random order in each of the following operations: preparation of the solid solutions of UO_2 with stabilizing additives, pressing and sintering of the plates of tungsten and UO_2 powder mixtures (five plates for each composition), roll bonding tungsten foil to the sintered plates, heat treatment to remove UO_2 particles exposed at the unclad edges, and thermal cycling (three specimens for each composition). This was done by assigning a number to each composition, plate, and specimen, and then using a table of random numbers to determine the order of processing.

The second part of the experimental work consisted of a comparison of thermal

cycling fuel loss results for completely clad (including the edges) W-UO_2 specimens containing 20 volume percent (12 weight percent) or 35 volume percent of UO_2 that was either unstabilized or stabilized with CaO or Y_2O_3.

Analyses of Materials

The ceramic grade UO_2 (of natural isotopic composition), CaO, Y_2O_3, ThO_2, and tungsten powders used in this study were obtained from commercial sources and were purported to be of high purity. Analyses for the impurities in these starting materials are listed in table I. In addition, an analysis of ceramic grade UO_2 after sintering is included. Some impurities, particularly carbon and silicon, appeared in the CaO and Y_2O_3 at undesirably high levels; however, analyses on each of the solid solutions (see table I) after sintering, grinding, and particle size classification showed that these impurities were present in tolerable amounts.

Preparation of Uranium Dioxide Materials

The solid solutions with the additives at the desired concentration levels were made by blending ceramic grade UO_2 and powdered additive, pressing into 200-gram cylindrical pellets at 75 000 pounds per square inch (5.2×10^8 N/sq m), and sintering in tungsten cups according to an atmosphere-temperature-time schedule given in reference 4. This schedule consisted of heating the pellets to 1100° C in helium (1 hr), holding at 1100° C in hydrogen (1/2 hr), raising the temperature to 2200° C in helium (3 hr), holding at 2200° C in helium (6 hr), and, finally, cooling to room temperature in helium. Phase diagrams indicating that UO_2-CaO, UO_2-ThO_2, and UO_2-Y_2O_3 form solid solutions in the ranges studied are shown in reference 5. Uranium dioxide without an additive was processed through the same sintering schedule.

After sintering, the pellets were ground between tungsten plates and classified to obtain a -270 to 400 mesh fraction of particles that were of irregular shape. The powders were analyzed to check on the impurity content, concentration of additive, solid solubility, crystal lattice dimensions, and the amount of tungsten introduced while preparing the solid solutions. These analyses are given in tables I and II.

Preparation of Specimens

The UO_2 powders were blended with tungsten powder to give a nominal composition of 35 volume percent UO_2. Cermets containing 20 volume percent UO_2 also were prepared in the cases of UO_2, UO_2 with 10 mole percent CaO, and UO_2 with 10 mole percent Y_2O_3.

TABLE I. - ANALYTICAL DATA ON MATERIALS USED

Species analyzed	Ceramic uranium dioxide	Calcium oxide	Yttrium dioxide	Thorium oxide	Tungsten	Uranium dioxide (sintered)	Uranium dioxide plus -		
							10 Mole percent calcium oxide	10 Mole percent yttrium oxide	10 Mole percent thorium dioxide
	Particle size, μ								
	0.5	3	1.3	0.58	0.88	30 to 60	30 to 60	30 to 60	30 to 60
	Concentration, ppm								
Aluminum	<1	300	----	<20	3	10	<1	<1	10
Boron	<.1	----	----	<.5	2	<.1	<.1	<.1	<.1
Barium	<10	----	20	----	<1	<10	<10	<10	<10
Beryllium	<1	----	----	<1	<1	<1	<1	<1	<1
Cobalt	<1	----	----	<5	<1	<1	<1	<1	<1
Chromium	<1	10	----	<10	7	10	5	10	5
Copper	.5	----	----	<6	5	10	2	1	2
Iron	10	600	20	<20	30	50	10	20	20
Magnesium	2	1000	----	<10	2	5	120	4	10
Manganese	<1	20	----	<10	<1	<1	<1	<1	<1
Nickel	<1	----	----	<10	10	10	<1	<1	5
Phosphorus	<50	----	<5	----	----	<50	<50	<50	<50
Silicon	2	4000	200	<50	15	5	5	<1	10
Zinc	------	----	----	<20	<1	<20	<20	<20	<20
Columbium	<.2	----	----	----	----	1.5	2.5	1.5	1.5
Hafnium	<1	----	----	----	----	<1	<1	<1	<1
Molybdenum	4	----	----	<10	30	1	3	3	10
Tantalum	<.5	----	----	----	----	1	2	2	1.5
Titanium	.2	10	----	<10	5	2	1	1	.8
Vanadium	<.2	----	----	<1	<1	.6	<.2	<.2	<.2
Zirconium	1	----	----	----	<1	2	4	6	4
Strontium	------	200	----	----	<1	-----	10	-----	-----
Fluorine	<1	15	8	10	45	<2	<2	<5	<2
Chloride[a]	17	<10	370	13	5	12	-----	30	14
Carbon	9	1300	1300	143	18	10	83	28	16
Sulfur	12	<10	<10	<10	----	6	<2	<2	4
Nitrogen	9	7	8	----	40	6	11	8	12
Calcium	------	----	2000	<10	15	5	-----	100	-----
Oxygen	------	----	----	----	3230	-----	-----	-----	-----
Oxygen-uranium ratio	2.22	----	----	----	----	2.06	-----	-----	-----

[a]Total halogens reported as chloride.

TABLE II. - COMPOSITION AND UNIT CELL DIMENSIONS OF URANIUM DIOXIDE SOLID SOLUTIONS

Additive	Nominal concentration of additive, mole percent	Analyzed amount of additive		Analyzed tungsten impurity in solid solution, weight percent	Average unit cell dimension, Å
		Weight percent	Mole percent		
Calcium oxide	2.5	0.55	2.7	1.45	5.4634
	5	1.00	4.8	1.67	5.4584
	10	2.08	9.5	2.12	5.4508
	15	3.27	13.9	.38	5.4327
Yttrium oxide	2.5	2.22	2.7	1.16	5.4555
	5	4.30	5.2	1.18	5.4474
	10	8.48	10.0	.82	5.4467
Thorium dioxide	2.5	2.33	2.4	1.57	5.4706
	5	4.86	5.0	1.58	5.4754
	10	9.77	10.0	1.32	5.4824

The procedure for making specimens consisted of the following steps (described in detail in ref. 6). Powder mixtures with 2 weight percent stearic acid added as a binder were pressed into 0.030-inch (0.076-cm) thick bars in a steel die and were sintered at 1750° C for 15 hours in dry, flowing hydrogen. Zirconium dioxide powder was used to separate the stacked plates during this process. After sintering and grinding to clean the surfaces, each plate was sandwiched between 0.003-inch (0.0076-cm) thick tungsten foils, heated in hydrogen to 1950° C, and rolled. The thickness of the plates was reduced by about 42 percent during this process, and an attempt was made to keep this constant for all the plates. Specimens were cut from the roll-clad plates after visual inspection and X-ray radiography. Figure 1 shows a photomicrograph of a cross section of a typical fabricated specimen. These specimens, designated as face-clad, had a tungsten cladding on the two major faces, but the edges were not clad. In the cases where specimens designated fully clad were required, either the edges of some face-clad specimens were covered with tungsten by plasma spraying (as described in ref. 7) or powder edge clad specimens were prepared by using a process developed at Lewis by G. K. Watson. Powder edge cladding was accomplished by first pressing W-UO_2 plates surrounded at the edges with tungsten powder and then sintering, grinding, and finally cladding the major faces of these plates with tungsten foil by hot rolling as described in reference 6. The tungsten powder used for the edge cladding was a blend of 30- to 60-micron particles and 0.88-micron particles in such proportion as to match the shrinkage of the W-UO_2 mixture during the sintering process. The two methods for preparation of fully clad speci-

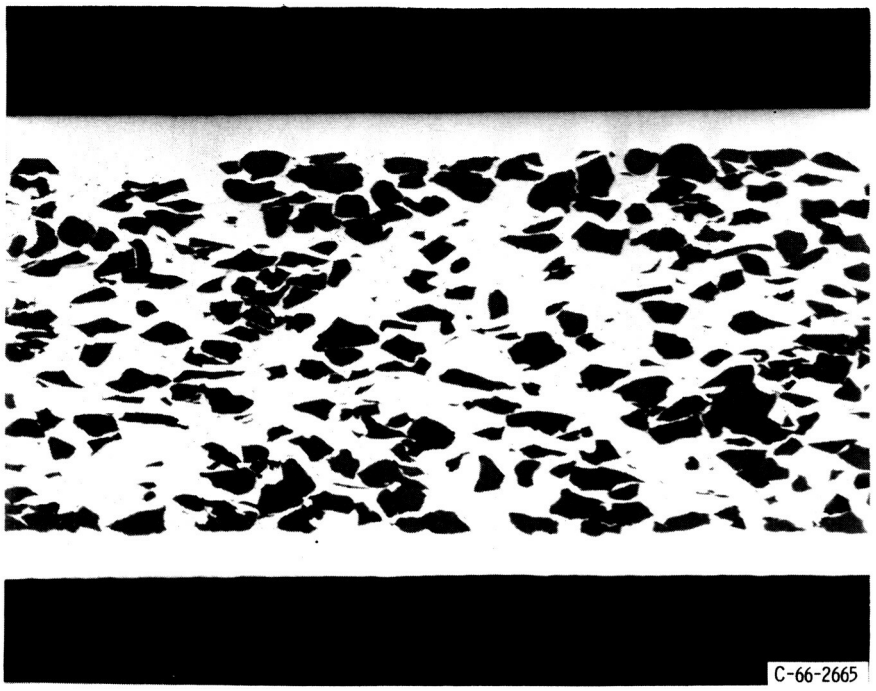


Figure 1. - Tungsten clad tungsten-uranium dioxide composite before thermal cycling. Yttrium oxide, 10 mole percent; uranium dioxide, 35 volume percent; as fabricated. X100.

mens gave slightly different fuel loss results; however, only one method was used on all specimens in any particular experiment.

The specimens were prepared for thermal cycling tests by heating to 1650° C for 30 minutes in hydrogen to remove surface oxides, weighing, heating six specimens at one time to 2500° C for 30 minutes in a purified hydrogen atmosphere flowing at 35 cubic feet per hour (~2.8×10^{-4} cu m/sec) under standard conditions to remove exposed UO_2 particles, and weighing each specimen again.

Testing of Specimens

Thermal cycling tests were carried out in an induction furnace in a stream (35 cu ft/hr under standard conditions) of dry, purified hydrogen at 1 atmosphere pressure. The temperature cycle involved a 1- to 2-minute rise time to 2500° C, a 10-minute hold at this temperature, and a temperature decrease to below 500° C in 1 to 2 minutes. A total of 10 to 15 minutes were allowed for additional cooling before the subsequent cycle was started. Six specimens, supported in a slotted tungsten holder, were run at one time. These were weighed before cycling and after 10, 15, 20, and 25 cycles. The fully clad specimens were cycled to as many as 220 cycles and weighed at least once every 10 cycles.

The percentage of fuel lost from each of the face-clad specimens during thermal cy-

cling was based on the combined weight loss of UO_2 and oxide additive present after the 30-minute heat treatment at 2500° C. The calculations were made by assuming that the weight loss was due entirely to volatilization of the solid oxide and that UO_2 and the additives were lost at rates proportional to the relative amounts of each originally present. The results were plotted as weight percent of oxide lost against the number of thermal cycles. In most cases each plotted point represents the average of three measurements.

PRESENTATION OF RESULTS

Table III gives the nominal composition of all the types of specimens tested as well as some average values for the weight percent of oxide lost after 25 thermal cycles to 2500° C in flowing hydrogen.

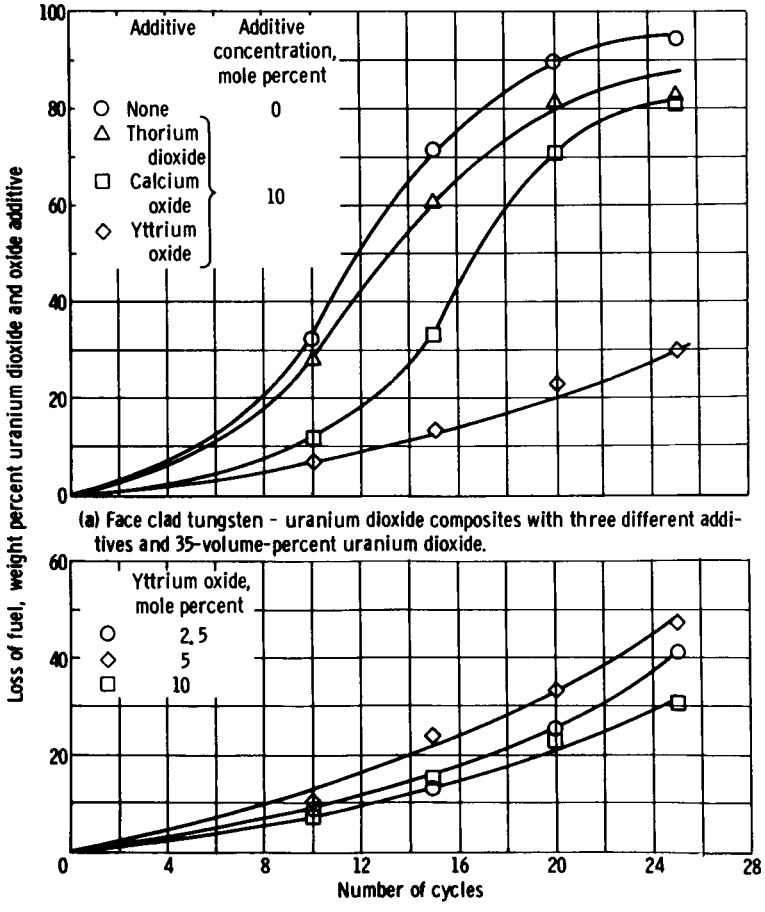
TABLE III. - FUEL LOSS FROM URANIUM DIOXIDE SOLID SOLUTIONS AFTER 25 CYCLES TO 2500° C IN HYDROGEN

Additive	Nominal concentration of additive, mole percent	Concentration of uranium dioxide in tungsten, volume percent	Type of cladding	Average fuel loss, percent
Calcium oxide	2.5	35	Face	95
	5	35	Face	96
	10	35	Face	81
	15	35	Face	77
Yttrium oxide	2.5	35	Face	41
	5	35	Face	48
	10	35	Face	30
Thorium dioxide	2.5	35	Face	94
	5	35	Face	90
	10	35	Face	81
None	----	35	Face	95
Calcium oxide	10	35	Full	4
Yttrium oxide	10	35	Full	1
	5	35	Full	1
	2.5	35	Full	~5
None	----	35	Full	~50
Calcium oxide	10	20	Full	2
Yttrium oxide	10	20	Full	<1
None	----	20	Full	35

The fuel losses from face-clad cermets containing 35 volume percent UO_2 with 10 mole percent ThO_2, CaO, Y_2O_3, or with no additive are compared in figure 2(a). Of the three additives, Y_2O_3 resulted in the lowest loss.

The effect of concentration of oxide added to the UO_2 (in this case, Y_2O_3) is depicted in figure 2(b) for face-clad specimens. The differences between the curves are relatively small and are not considered to be significant in view of the scatter generally observed in such data.

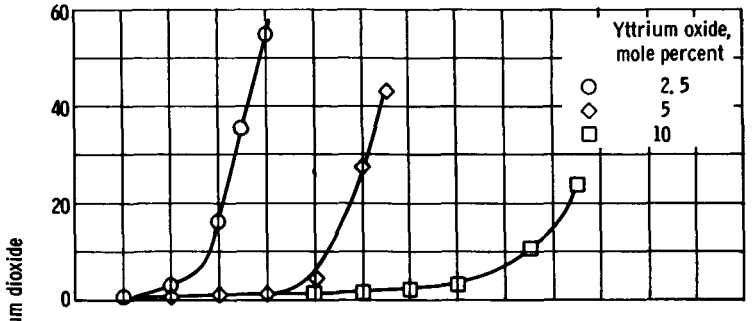
It is especially important to know how fuel loss varies as a function of concentration of additive because the total amount of oxide in the cermet must be kept as low as possible to avoid loss of strength in the composite (ref. 8). The UO_2 loading is fixed by the



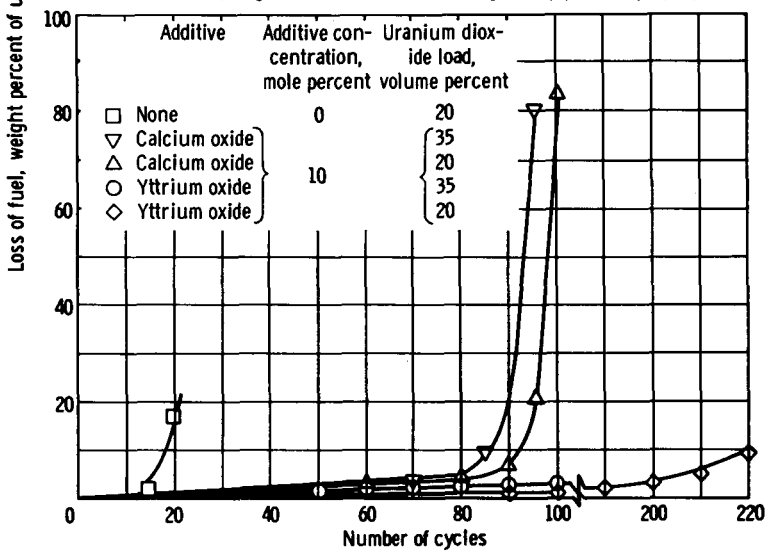
(a) Face clad tungsten - uranium dioxide composites with three different additives and 35-volume-percent uranium dioxide.

(b) Face clad tungsten - uranium dioxide composites containing yttrium oxide additive and 35-volume-percent uranium dioxide.

Figure 2. - Effect of different additives and of additive concentration on fuel loss from tungsten - uranium dioxide composites thermally cycled to 2500° C in hydrogen at flow of 35 standard cubic feet per hour and 1 atmosphere pressure. Overall size of composites, 1.4 by 1.0 by 0.018 inch; cladding thickness, approximately 0.0018 inch tungsten on faces; cycle duration, 10 minutes.



(c) Fully clad composites containing yttrium oxide additive and 35-volume-percent uranium dioxide; edges clad with 0.05-inch tungsten by plasma spraying.

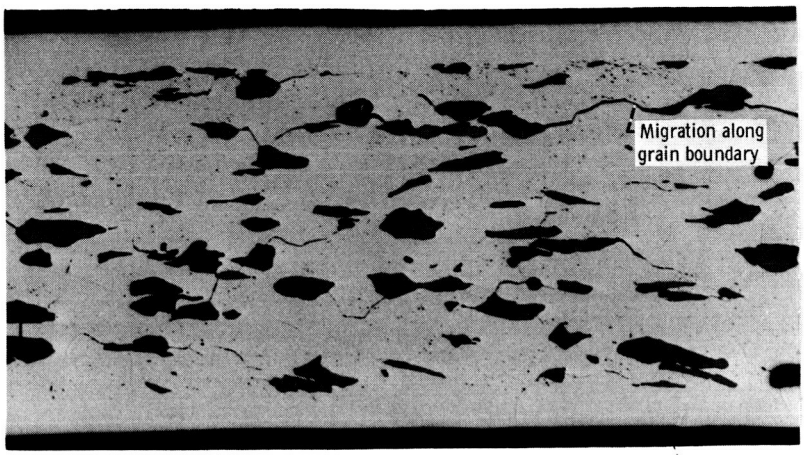


(d) Fully clad composites with different uranium dioxide loadings containing calcium oxide or yttrium oxide additive; edges clad with 0.2-inch tungsten by powder sintering.

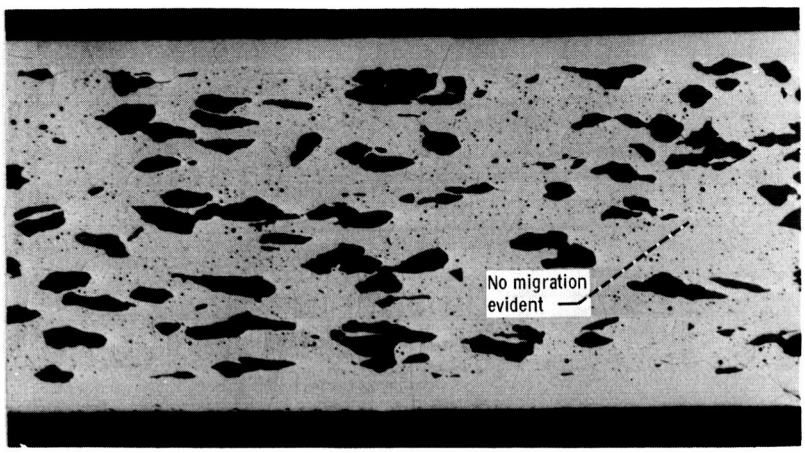
Figure 2. - Concluded.

reactor design; however, no more than the necessary amount of oxide stabilizer should be added so that the composite strength can be maintained. Since the results on face-clad specimens were inconclusive (possibly because of the exposed edges, as will be discussed later) several thermal cycling runs were carried out on face-clad specimens containing Y_2O_3 additives (nominally 2.5, 5, and 10 mole percent with UO_2) with the edges coated with tungsten by plasma spraying. According to the results shown in figure 2(c), 10 mole percent of Y_2O_3 in the UO_2 gave the longest life. Ten mole percent was the highest concentration of Y_2O_3 studied and results in a total ceramic loading of about 42 volume percent for a UO_2 loading of 35 volume percent.

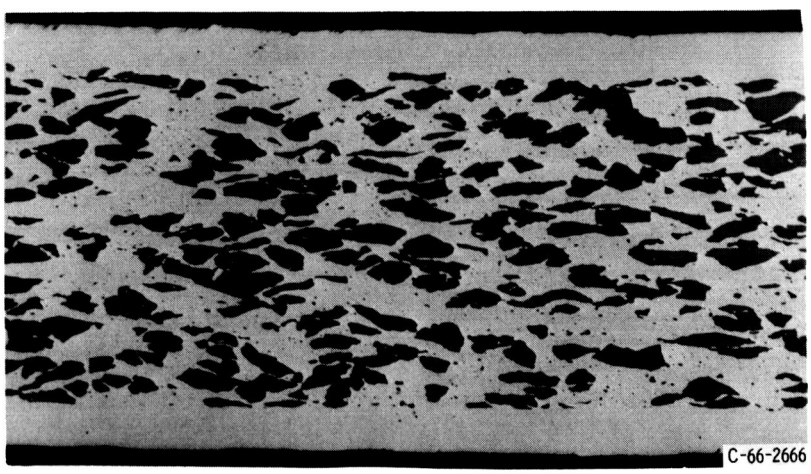
Fully clad (powder edge clad) specimens containing 20 or 35 volume percent of UO_2 unstabilized or stabilized with 10 mole percent Y_2O_3 or CaO were cycled to compare the effects of both fuel loading and kind of additive, independent of edge effects. It can be noted from figure 2(d) that cermet specimens containing 35 volume percent UO_2 plus



(a) Calcium oxide concentration, 10 mole percent; uranium dioxide load, 20 volume percent; fuel loss, 2.5 weight percent.



(b) Yttrium oxide concentration, 10 mole percent; uranium dioxide load, 20 volume percent; fuel loss, 0.5 weight percent.



(c) Yttrium oxide concentration, 10 mole percent; uranium dioxide load, 35 volume percent; fuel loss, 0.7 weight percent.

Figure 3. - Photomicrographs of fully clad stabilized tungsten-uranium oxide composites after 25 10-minute cycles to 2500° C in flowing hydrogen. X100.

10 mole percent Y_2O_3 in solid solution and fully clad with tungsten showed a weight loss of about 1 percent of the UO_2 originally present after 25 ten-minute thermal cycles to 2500° C in flowing, purified hydrogen. Accelerated loss did not occur during the 100-cycle test carried out on the specimens. Similar specimens containing CaO rather than Y_2O_3 and tested under the same conditions lost more fuel throughout the thermal cycling procedure, and accelerated loss began after 80 cycles. Evidence for fuel migration after 25 thermal cycles is given by microstructures of specimens in figure 3. Specimens containing 20 volume percent UO_2 show little or no migration of UO_2 into the tungsten grain boundaries when stabilized with 10 mole percent Y_2O_3 but extensive migration when stabilized with 10 mole percent CaO. Specimens containing a fuel loading of 35 volume percent UO_2 stabilized with 10 mole percent Y_2O_3 also show little or no migration of the fuel after 25 cycles to 2500° C in flowing purified hydrogen.

DISCUSSIONS OF RESULTS AND MECHANISMS

The most important results are:

(1) Y_2O_3, CaO, and ThO_2 in solid solution with UO_2 stabilize W-UO_2 composites against uranium loss during thermal cycling.

(2) The effectiveness of the additive oxides at equivalent concentrations in UO_2 decreased in the order Y_2O_3, CaO, and ThO_2.

(3) Of the concentrations of Y_2O_3 tested, the decreasing order of the effectiveness is 10, 5, and 2.5 mole percent.

These results are discussed in the light of what is known about the decomposition of unstabilized UO_2 composites during thermal cycling to 2500° C in hydrogen.

Decomposition of Uranium Dioxide

Two successive reactions of unstabilized UO_2 contribute to the loss of uranium from W-UO_2 composites under thermal cycling conditions. First, at high temperatures (e.g., at 2500° C), the UO_2 loses oxygen to become substoichiometric in oxygen:

$$UO_2 \rightleftarrows UO_{2-x} + x[O]$$

The substoichiometric oxide retains the fluorite structure of UO_2; however, the structure has vacant oxygen sites compensated by reduced U^{4+} ions. Reference 9 shows that, as the value of x increases, the substoichiometric UO_2 becomes more difficult to reduce further. This result is shown quantitatively in figure 4 (from ref. 9) by a plot of the partial molar free energy of oxygen in UO_2 as a function of oxygen-uranium ratio (O/U). In

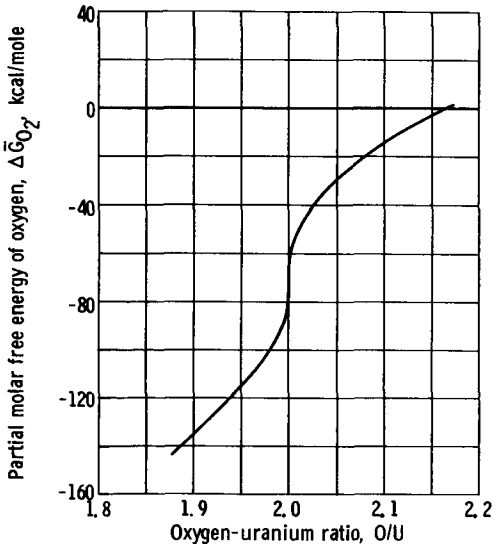


Figure 4. - Partial molar free energy of oxygen in uranium dioxide at 2400° C plotted against oxygen-uranium ratio (from ref. 9).

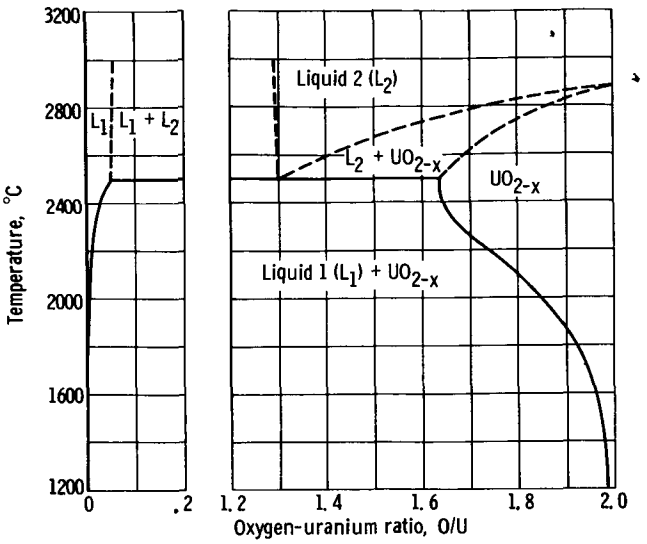


Figure 5. - Uranium-oxygen phase diagram (from ref. 10).

interpreting this plot, it should be noted that decreasing values of the free energy indicate increasing stability to further reduction. The second reaction, which occurs upon cooling, can be represented as follows:

$$UO_{2-x} \rightleftharpoons \left(1 - \frac{x}{2}\right)UO_2 + \frac{x}{2}U$$

A phase diagram showing a plot of the temperature composition boundary where this reaction occurs is presented in figure 5 (from ref. 10). The free uranium metal resulting from this reaction migrates readily through the tungsten grain boundaries of a W-UO_2 composite and leads to grain boundary cracking and mechanical degeneration of the composite.

Role of Oxide Stabilizers

The stabilization of UO_2 by additions of CaO or Y_2O_3 can be related, in part, to the presence of oxygen vacancy defects in the lattices of the solid solutions. In the range of concentrations studied, the solid solutions maintain the fluorite structure of unstabilized UO_2; however, since the cation valences of the additives are less than that of the uranium (+2 for calcium and +3 for yttrium compared with +4 for uranium), oxygen vacancies are introduced into the lattice to compensate for the lower valence of the additive cations. Thus, by substitution of Ca^{2+} or Y^{3+} ions for some of the U^{4+} ions, oxygen vacancies can

be introduced into the fluorite lattice without any corresponding reduction of U^{4+}. Although partial molar free energy data for oxygen in UO_2-CaO or UO_2-Y_2O_3 solid solutions are not available, it is hypothesized that oxygen-deficient UO_2 and the solid solutions are similar in regard to their increased stabilities toward reduction. In the case of the solid solutions, however, this increased stability can occur without the formation of free uranium metal during cooling.

Since addition of ThO_2 to UO_2 does not introduce vacancies, the stabilization of UO_2 by ThO_2 cannot be accounted for by this vacancy model. The somewhat lower fuel loss from the ThO_2-stabilized composites could be explained either by the possibility that the molar free energy for oxygen in UO_2-ThO_2 solid solutions is slightly lower than that for oxygen in pure UO_2 or by the lower volatility of UO_2-ThO_2 compared with UO_2. Since the effectiveness of additives like CaO and Y_2O_3 appears to be potentially much greater than that of ThO_2, ThO_2 will not be discussed further.

Comparison of Yttrium Oxide and Calcium Oxide as Additives

The oxygen vacancy defect explanation is not sufficient to account for the observation that Y_2O_3 has a greater stabilizing effect than CaO at the same mole percentage concentration in UO_2. Although CaO introduces a slightly larger number of vacancies in UO_2 than Y_2O_3 does at the same mole percentage concentration, it confers less stability to the UO_2 (see figs. 2(c) and (d) (p. 9)). (For nominal and analyzed concentrations of additives, see table II (p. 5), and for the calculated number of vacancies for these concentration levels, see table IV.)

Along with the fact that the partial molar free energy of oxygen in the solid solution is not necessarily a simple function of the oxygen vacancy concentration alone, two other possibilities exist that could account for the relative effectiveness of CaO and Y_2O_3 as additives.

One possibility is that the solid solutions oxidize to different degrees. It has been shown (refs. 11 and 12) that UO_2 with Y_2O_3 in solid solution readily takes up oxygen. This oxygen probably fills vacancies. Reference 13 shows that UO_2-Y_2O_3 appears to have a greater tendency than UO_2-CaO to pick up oxygen.

The oxygen-metal ratio was not controlled during this present work, and because of the lack of a suitable analytical method, it was not determined in completed composite specimens. It is therefore conceivable that the oxygen-metal ratio was somewhat in excess of the stoichiometric value and was different for UO_2-Y_2O_3 and UO_2-CaO. (If the oxygen-metal ratio exceeds a value where the oxygen activity is high enough to form tungsten oxides, these oxides can react with UO_2 to form a ternary eutectic in the UO_2-U_xWO_3-W region which has a melting point as low as 1300° C (ref. 14). It is believed that the oxygen-metal ratio did not become high enough under the conditions used

TABLE IV. - EFFECT OF VARIOUS AMOUNTS OF YTTRIUM OXIDE AND CALCIUM OXIDE ON THE OXYGEN-METAL RATIO AND DEFECT SITE CONCENTRATION IN STOICHIOMETRIC SOLID SOLUTIONS WITH URANIUM DIOXIDE

Additive, mole percent	Oxygen-metal ratio, O/M	Fraction of oxygen sites unoccupied	Fraction of uranium ion sites occupied by additive ions
Solid solution with calcium oxide			
0	2.000	0	0
2.5	1.975	.012	.025
2.7	1.973	.014	.027
4.8	1.952	.024	.048
5.0	1.950	.025	.050
9.5	1.905	.048	.095
10.0	1.900	.050	.100
13.9	1.861	.070	.139
15.0	1.850	.075	.150
Solid solution with yttrium oxide			
0	2.000	0	0
2.5	1.976	.012	.049
2.7	1.974	.013	.053
5.0	1.952	.024	.095
5.2	1.951	.024	.099
10.0	1.909	.046	.184

in this work to form any significant amount of eutectic.) Since reduction of UO_2 in W-UO_2 composites during thermal cycling to 2500° C in hydrogen requires transport of oxygen-rich reaction products through the tungsten matrix, the presence of excess oxygen in the stabilized UO_2 can delay the formation of free uranium. The greater effectiveness of a complete tungsten cladding compared with a face cladding (see figs. 2(a) and (d)) in reducing thermal cycling fuel loss supports the idea that transport of oxygen-rich reaction products through tungsten is a critical rate controlling step.

Another possibility is that Y_2O_3 volatilizes less readily than CaO from solid solutions with UO_2 when composites are thermally cycled to high temperatures. Experiments (refs. 13 and 15) show that solid solutions of Y_2O_3 in UO_2 are less volatile than solid solutions of CaO in UO_2 at high temperatures (e.g., 2500° C). The experiments on solid solutions of CaO in UO_2 showed that CaO decreased in concentration in the residual fuel after high-temperature treatment.

Effect of Additive Concentration

To understand how the concentration of additive determines the thermal cycling life in face-clad and in fully clad specimens, the rate of loss of oxygen-rich reaction products must be compared. In the case of the face-clad specimens, these products are readily lost at the unclad edges, which leads to the formation of free uranium and subsequent fuel migration and to the early onset of volatilization losses at the unclad edges. These losses due to volatilization tend to obscure the difference in stability of the UO_2 as a function of Y_2O_3 or CaO concentration over the range studied. The rate at which reaction products are lost from fully clad specimens depends on the characteristics of the cladding (e. g., thickness, purity, grain structure, and porosity), which are assumed to be constant in this experiment, and on the partial pressure of the reaction products. Volatilization becomes important only when the cladding has been opened at the grain boundaries. The concentration of the additive determines the partial pressures of the reaction products and, therefore, determines their rates of diffusion through the tungsten cladding and the onset of fuel decomposition. Thus, in fully clad composites, the stabilizing effect of the additives is expected to increase with their concentration. This behavior was observed.

CONCLUSIONS

The results of thermal cycling tests on face-clad and fully clad tungsten - uranium dioxide (W-UO_2) composites containing UO_2 stabilized with thorium dioxide (ThO_2), calcium oxide (CaO), or yttrium oxide (Y_2O_3) have led to the following conclusions:

1. Loss of fuel during thermal cycling of W-UO_2 composites in flowing purified hydrogen for specimens containing 35 volume percent of UO_2 was reduced by the use of ThO_2, CaO, or Y_2O_3 as additives to the UO_2. Among these additives, Y_2O_3 gave the best results.

2. The stabilization of UO_2 by CaO or Y_2O_3 in solid solution can be explained in part on the basis of the oxygen vacancies introduced into the fluorite lattice. This explanation, however, does not account for the difference in effectiveness of CaO and Y_2O_3 as stabilizers or for the stabilizing effect of ThO_2.

3. Fuel loss data from fully clad specimens showed that the stability of W-UO_2 composites improved with increasing Y_2O_3 concentration in the UO_2.

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