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AN INVESTIGATION OF SOME VARIABLES AFFECTING AND METHODS OF INHIBITING THERMAL-CYCLIC FUEL LOSSES FROM TUNGSTEN - URANIUM DIOXIDE COMPOSITES

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Cleveland, Ohio

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AN INVESTIGATION OF SOME VARIABLES AFFECTING AND METHODS OF INHIBITING THERMAL-CYCLIC FUEL LOSSES FROM TUNGSTEN - URANIUM DIOXIDE COMPOSITES (U)

by Michael A. Gedwill

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SUMMARY

The effects of some test variables on the thermal-cyclic fuel (uranium dioxide) losses from partly clad tungsten - uranium dioxide ($W-UO_2$) composites were studied as part of the NASA water-moderated, nuclear-rocket-reactor program. The composites for most of these studies were subjected to thermal cycles between ambient temperatures (about 20° C) and 2500° C in a flowing hydrogen atmosphere. Several methods of reducing the effects of thermal-cyclic fuel losses from partly clad and completely clad $W-UO_2$ composites were also studied.

A considerable increase in the rate of fuel loss (fuel loss per cycle) from partly clad composites resulted from either (1) cycling exclusively in hydrogen rather than in duplex-atmosphere environments (i.e., use of either hydrogen or helium within various temperature ranges), (2) an increase in the maximum cycling temperature from 2200° to 2500° C, or (3) an increase in fuel loading. The increase in the rate of fuel loss from these composites during thermal cycling in hydrogen is attributed primarily to (1) decomposition of UO_2 to UO_{2-x} (i.e., oxygen-deficient UO_2) at elevated temperatures and subsequent disproportionation of UO_{2-x} to uranium and UO_2 at intermediate temperatures followed by uranium hydride formation at lower temperatures, (2) migration of uranium during successive heating and cooling cycles, (3) the high rates of migration and vaporization of the decomposition and reaction products at elevated temperatures, (4) the large difference in the thermal expansivities of tungsten, uranium, and UO_2, and (5) the higher probability of interconnection of fuel particles at high fuel loadings.

The high rates of fuel loss resulting from cycling partly clad composites in hydrogen were substantially reduced by three methods. In the order of increasing effectiveness, these methods were (1) small additions of fine thorium dioxide particles to the tungsten matrix, (2) use of fine (less than 1 μ) UO_2 fuel particles instead of large (50 μ) fuel particles, and (3) additions of metal oxides in solid solution with UO_2. A further reduction in these rates was realized with the use of completely clad composites.

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INTRODUCTION

One nuclear-rocket-reactor concept that has been under investigation at the NASA Lewis Research Center consists of a tungsten, water-moderated, thermal-reactor system. In this concept (described in ref. 1), the reactor system is to employ tungsten-clad fuel elements containing about 10 to 35 volume percent of uranium dioxide (UO_2) dispersed in tungsten matrices as the heat source for the hydrogen propellant. This reactor system is to operate at temperatures up to at least 2500° C in a rapidly flowing, high-pressure hydrogen atmosphere. In addition, several cyclic shutdowns and restarts of the reactor are anticipated for a space mission; during shutdowns, the reactor will probably be exposed to the hard vacuum of space. Therefore, W-UO_2 composites must be evaluated under a variety of conditions, such as thermal cycling, changes in atmosphere (hydrogen and vacuum), and varying hydrogen pressure and flow conditions.

Results from a previous study of the fuel retention properties of W-UO_2 composites (reported in ref. 2) showed that thermal cycling of these composites between ambient temperatures (about 20° C) and 2500° C in a hydrogen atmosphere produced catastrophic fuel (UO_2) losses with accompanying structural deterioration of the composites. Preliminary results on methods of inhibiting the thermal-cycling-induced fuel migration in W-UO_2 composites were also reported in reference 2. More recently, very promising results of inhibiting fuel loss under thermal cycling conditions by solid-solution additions to the UO_2 were reported in reference 3.

The purposes of the investigation reported herein were (1) to study the effects of several thermal-cyclic test variables in more detail, and (2) to study further possible methods of reducing the detrimental effects of thermal cycling. To this end, the effects of test variables such as time, temperature, atmosphere, fuel loading, composite size, etc., were evaluated. Based on the results of these studies and the expected reactor operating conditions, a reference thermal-cycling procedure was established and used in testing the effectiveness of three different methods of retarding fuel decomposition.

EXPERIMENTAL PROCEDURE

Materials

The particle size and chemical analyses of the as-received powders are included in table I. High-fired UO_2 powder, which was depleted of the uranium 235 isotope, was used in most of the studies described in this report. Micron-size and ceramic-grade UO_2 powders, which contained naturally occurring concentrations of uranium 235 and uranium 238 isotopes, however, were used in the studies to determine the effects of

fuel particle size and metal-oxide additions (thorium dioxide (ThO_2), calcium oxide (CaO), and zirconium dioxide (ZrO_2)) in solid solution with UO_2, respectively. The ThO_2 powder was also used in a study to determine the effect of ThO_2 additions to the tungsten matrix.

Solid solutions of UO_2 (ceramic grade) containing nominally 10 mole percent additions of either ThO_2, CaO, or ZrO_2 were prepared by blending and pressing the powders followed by sintering at 2200° C in flowing helium. The sintered compacts were crushed and screened into powders in a size range of -270/+400 mesh (about 50 μ). Preparation of the solid-solution powders is described in detail in reference 3. The solid solutions were chemically analyzed for the additive elements, which were found to be present in the desired amounts as the oxides. Debye powder patterns of these materials showed only an expanded or contracted UO_2 lattice with no other lines discernible, except tungsten, thus indicating solid solubility of the additive oxides in UO_2. The tungsten lines were a result of pickup of tungsten, which occurred during the crushing of the compacts between tungsten plates.

Composite Fabrication

Composites were fabricated by blending, pressing, and sintering the powders followed by roll cladding according to the method described in reference 4. The composites were sintered at 1750° C and roll clad with tungsten at about 1950° C in hydrogen. For most of these studies, the composites were clad with tungsten foil (about 0.002 in. (0.005 cm) in thickness after rolling) on only the two major surfaces with the edges being unclad. The composites were cut into rectangular samples (nominally, $1\frac{3}{8}$- by 1- by 0.021 in. (3.5- by 2.5- by 0.053 cm)) for testing. In this report, these composites will be referred to as partly clad composites. Completely clad composites were similarly fabricated with tungsten foil-clad surfaces, but also with the tungsten powder-clad edges. Briefly, the fabrication of these composites consisted of using tungsten powder around the W-UO_2 cores in a picture-frame arrangement prior to pressing, sintering, and roll cladding. The foil-clad and powder-clad thicknesses were about 0.002 inch (0.005 cm) and 0.2 inch (0.5 cm), respectively.

Apparatus and Testing

The thermal-cyclic tests were conducted in a ZrO_2 insulated induction furnace (described in ref. 5) that contained a tungsten susceptor and tungsten and molybdenum radiation shields. Gas flow rates of 35 standard cubic feet per hour (0.28 liter/sec) of hydrogen or 25 standard cubic feet per hour (0.20 liter/sec) of helium were employed

[redacted]

TABLE I. - PARTICLE SIZE AND CHEMICAL AND SPECTROGRAPHIC ANALYSIS OF STARTING POWDERS

Element	Uranium dioxide			Tungsten	Thorium dioxide	Calcium oxide	Zirconium dioxide
	Grade						
	High fired	Micron size	Ceramic grade				
	Fischer particle size, μ						
	50	0.58	0.49	0.88	0.58	3.01	6.80
Chemical analysis, ppm[a]							
Carbon	25	13	9	30	143	1300	----
Fluorine	[b]<1	7	<1	<1	10	15	----
Halogens[c]	43	15	17	5	13	2	----
Nitrogen	16	11	9	40	13	----	----
Oxygen	------	------	------	3230	---	----	----
Sulfur	<1	16	12	<5	<10	<10	----
Thorium	16	7	31	-------	---	----	----
Uranium	88.09%	87.45%	86.52%	-------	---	----	----
Oxygen to uranium atoms	2.001	2.14	2.22	-------	---	----	----
Spectrographic analysis, ppm[a]							
Aluminum	160	10	<1	<2	<20	300	2000
Antimony	<1	<1	<1	-------	-----	----	----
Arsenic	<30	<30	<30	<100	-----	----	----
Barium	<10	<10	<10	<1	-----	----	----
Beryllium	<.1	<1	<1	<.1	<1	----	----
Boron	<.1	<.1	<.1	<.1	<.5	----	----
Bismuth	<1	<1	<1	-------	-----	----	----
Calcium	1	1	1	1	<10	----	4800
Cadmium	<.1	<.1	<.1	<1	<.5	----	----
Cesium	<10	<10	<10	<1	-----	----	----
Chromium	<1	<1	<1	.5	<10	10	----
Cobalt	<5	<1	<1	<.01	<5	----	----
Columbium	2	.5	<.2	-------	<50	----	----
Copper	.2	.5	.5	.05	<6	----	----

[a]By weight unless otherwise indicated.

[b]<Not detected with limits of detection as indicated.

[c]Calculated as chlorine.

[redacted]

[redacted]

TABLE I. - Concluded. PARTICLE SIZE AND CHEMICAL AND SPECTROGRAPHIC ANALYSIS OF STARTING POWDERS

Element	Uranium dioxide			Tungsten	Thorium dioxide	Calcium oxide	Zirconium dioxide
	Grade						
	High fired	Micron size	Ceramic grade				
	Fischer particle size, μ						
	50	0.58	0.49	0.88	0.58	3.01	6.80
Spectrographic analysis, ppm[a]							
Gallium	<1	<1	<1	------	-----	----	----
Germanium	<1	<1	<1	------	-----	----	----
Gold	<1	<1	<1	------	-----	----	----
Hafnium	<1	<1	<1	------	-----	----	----
Indium	<3	<3	<3	------	-----	----	----
Iron	12	50	10	6	<20	300	3000
Lead	<3	<3	<3	<.01	<2	30	----
Lithium	<1	<1	<1	<1	-----	----	----
Magnesium	.1	40	2	.2	<10	1000	7000
Manganese	3	<1	<1	<.1	<10	20	30
Mercury	<1	<1	<1	------	-----	----	----
Molybdenum	50	1	4	3	<10	----	----
Nickel	1	5	<1	1	<10	----	----
Phosphorous	<50	<50	<50	------	<5	----	----
Potassium	<5	<5	<5	70	10	20	----
Rubidium	<10	-----	<10	1	-----	----	----
Silicon	45	5	2	3	<50	4000	6200
Silver	.1	.1	<.1	<1	-----	----	----
Sodium	1	3	10	50	<20	50	10
Strontium	<1	-----	-----	<1	-----	200	----
Tantalum	<.5	<.5	<.5	------	-----	----	----
Thallium	<2	<2	2	------	-----	----	----
Tin	<.5	<.5	<.5	<.01	<2	----	----
Titanium	.2	2	.2	<.1	<10	10	660
Tungsten	4	15	2	------	-----	----	----
Vanadium	<.2	1.5	<.2	.08	<1	----	----
Zinc	<2	15	-----	1	<20	----	----
Zirconium	75	1	1	1	<10	----	----

[a]By weight unless otherwise indicated.

[redacted]

for a furnace volume of about 0.026 cubic foot (0.74 liter). Tank-grade (99.9 percent minimum purity) hydrogen and helium gases were used, but these were purified before being supplied to the furnace, as described in reference 2. The moisture and oxygen contents in both gases on entering the furnace were analyzed and found to be less than 15 and 3 parts per million by volume, respectively. Temperature measurements were made by sighting a micropyrometer onto a blackbody hole in a tungsten block, which was placed in the furnace adjacent to the composites. The estimated accuracy of the temperature measurements was $\pm 25^{\circ}$ C at 2500° C.

Each composite was treated prior to testing to remove spurious surface contaminants that may introduce errors in the measurements of fuel losses resulting from testing. This treatment consisted of ultrasonically cleaning the composite in ethyl alcohol for several minutes followed by heating for 1/2 hour in hydrogen at 1650° C.

The thermal-cycling test procedure employed in these studies consisted of subjecting several composites simultaneously to a number of heat treatments (cycles) at the test temperature, each for a constant time (test duration) with intermittent cooling to ambient temperatures (about 20° C). The composites, however, were spaced to prevent shielding of adjacent composites from exposure to the atmosphere. In order to ensure complete cooling, the composites were held at ambient temperatures for at least 10 minutes between reheats. Heating and cooling periods were about 10 minutes (between ambient temperatures and the test temperature) during testing, unless otherwise indicated.

Evaluations

The effects of the test variables and the effectiveness of the three methods of reducing fuel losses were evaluated primarily on the basis of fuel-loss calculations. These calculations involved weight measurements to within 0.1 milligram before and after testing. The resultant weight losses for the tested composites were represented as a result only of UO_2 losses because similarly fabricated and tested unfueled tungsten composites showed no measurable weight changes. In some instances, average fuel losses are presented herein for those composites tested in duplicate or triplicate. The magnitudes of the fuel losses reported are very dependent on the geometry of the composite; cladding is particularly important. Although the effects reported are believed to be generally applicable to W-UO_2 composites, no attempts should be made to compare the magnitudes of the fuel losses reported herein with data from other studies using composites of different geometries.

Cross sections of the composites were metallographically examined before and after testing to determine the effects of testing on the microstructures. Metallographic prep-

aration consisted of mounting the composites in epoxy after cutting, grinding the cut surfaces on 240-, 400-, and 600-grit silicon carbide papers with water as a lubricant, followed by vibratory polishing with 0.3-micron alumina on nylon cloths for rough polishing and with 0.1-micron alumina on deep-nap cloths for fine polishing. In most instances, the cross sections were examined in the unetched (as-polished) and etched conditions; Murakami's reagent was used as the etching solution. Several tested composites were analyzed in an electron microprobe analyzer.

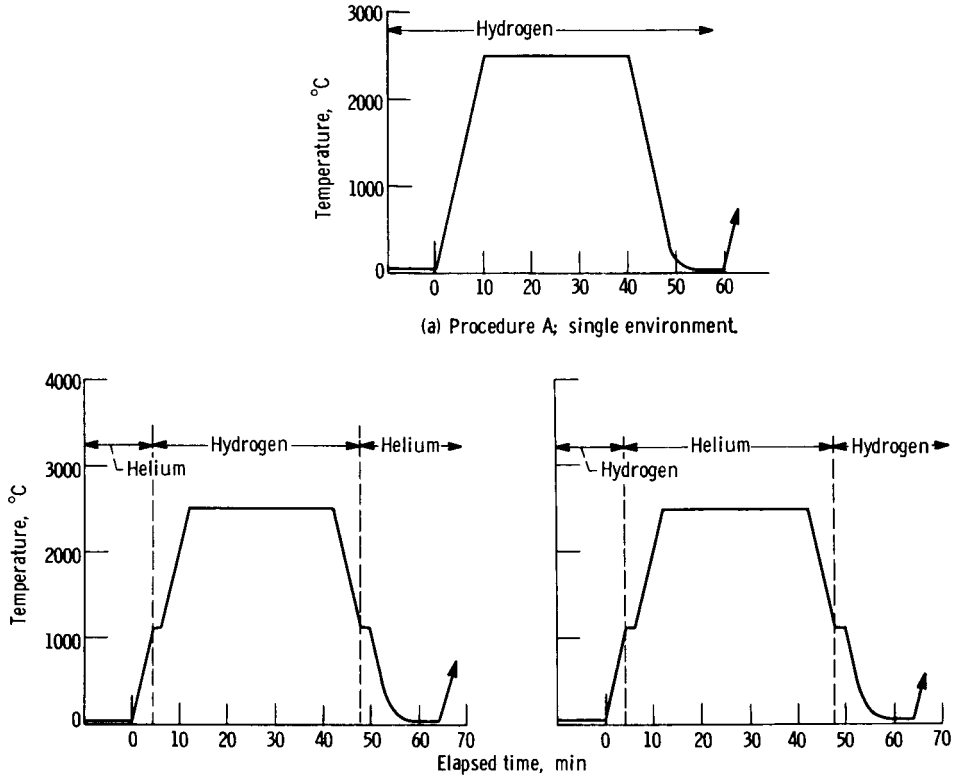
RESULTS

Effect of Test Variables on Thermal-Cyclic Fuel Losses from W-UO_2 Composites

Atmosphere. - Initial data on the effect of test atmosphere on the amount of fuel lost from W - 20-volume-percent UO_2 composites tested for 1-hour durations at 2500° C were presented in a previous report (ref. 2). In that study, the composites were cycled exclusively between ambient temperatures and 2500° C in either hydrogen, helium, or vacuum. The fuel-loss data showed that the rate of fuel loss (fuel loss per cycle) was low and constant throughout the test in helium, but increased rapidly during cycling in hydrogen. The behavior in vacuum, however, was intermediate to that in helium and hydrogen; the rate of fuel loss was low and constant for several cycles, but then increased rapidly. Metallographic examination of the helium tested composite showed some evidence of fuel migration through the grain boundaries of the tungsten matrix, while the vacuum-tested composite showed significantly more fuel migration throughout the matrix and also, to a slight extent, in the cladding. The hydrogen tested composite showed the presence of an additional phase, primarily at the W-UO_2 particle interfaces, and extensive fuel migration throughout both the matrix and cladding. Electron microprobe analyses and metallographic evaluations indicated that this additional phase was highly rich in uranium (probably uranium metal), and the fuel in the tungsten grain boundaries was essentially UO_2. Other investigators (refs. 6 to 12) have observed and identified uranium metal in UO_2 pellets that had been heated at temperatures of 1800° C and above in either hydrogen, vacuum, or inert atmospheres.

In order to obtain a better understanding of the fuel-loss mechanism, composites were cycled exclusively in either hydrogen or in duplex-atmosphere environments (i.e., use of either hydrogen or helium within various temperature ranges). The environments and temperature ranges are schematically illustrated in figure 1 for 1 thermal cycle. The composites tested in the duplex-atmosphere environments (figs. 1(b) and (c)) were held at 1100° C for 1 to 2 minutes to allow changeover of the atmospheres, which was accomplished by flushing with the second gas. Figure 2 shows the fuel-loss

[redacted]



(a) Procedure A; single environment.

(b) Procedure B; duplex environment.

(c) Procedure C; duplex environment.

Figure 1. - One thermal cycle for single- and duplex-atmosphere environments.

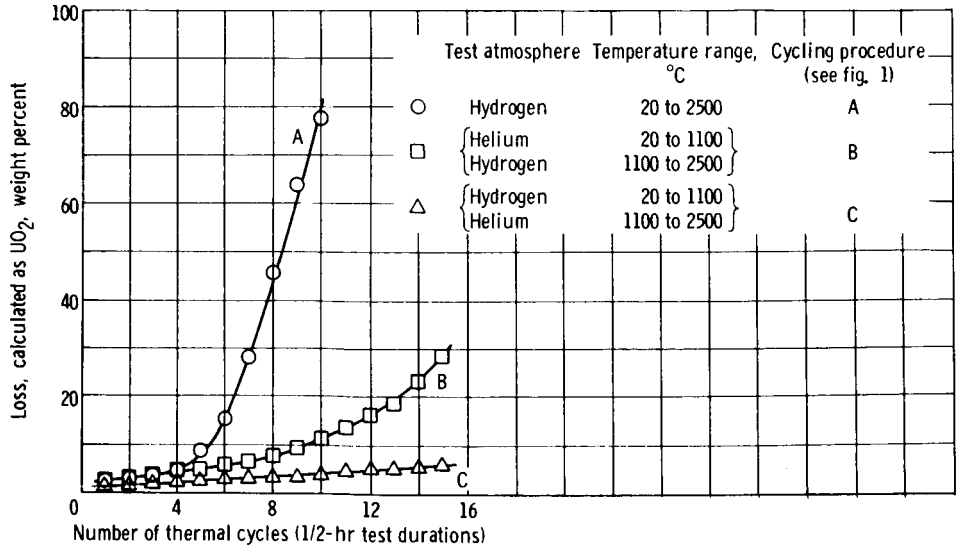


Figure 2. - Effect of single and duplex-atmosphere environments on thermal cycling of tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments of 2500° C with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

[redacted]

[redacted]

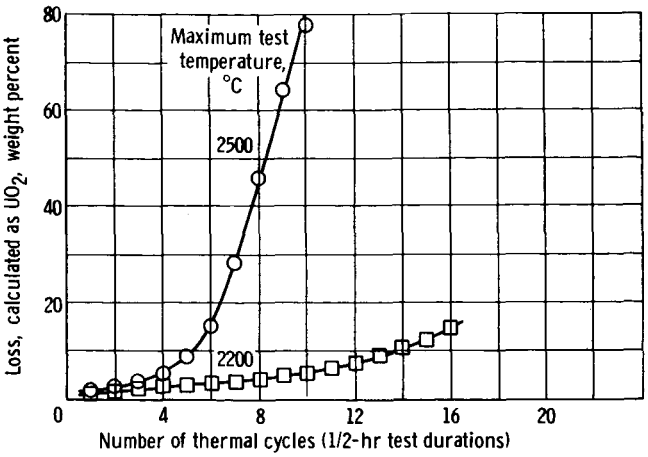


Figure 3. - Effect of test temperature on thermal-cyclic behavior of tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments at either 2200° or 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperature. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

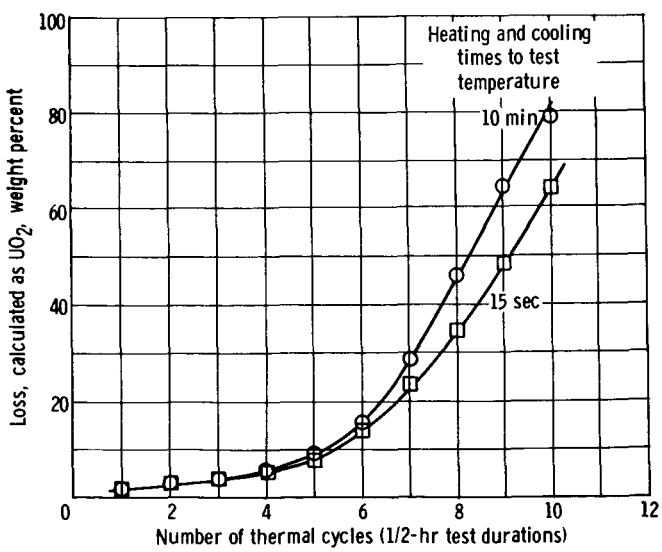


Figure 4. - Effect of heating and cooling rates on thermal-cyclic behavior of tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

data of W - 20-volume-percent UO_2 composites tested for 1/2-hour durations at 2500° C in the three environments illustrated in figure 1. Comparison of the fuel losses represented by curves A and B shows that the rate of fuel loss in hydrogen was substantially reduced when composites were heated and cooled in helium below 1100° C. However, high-temperature treatments in helium with low-temperature treatments in hydrogen (curve C) resulted in the lowest rate of fuel loss up to fifteen 1/2-hour cycles.

Temperature. - The effect of maximum thermal cycling temperature is illustrated in figure 3 that shows the fuel-loss results of W - 20-volume-percent UO_2 composites cycled for 1/2-hour durations at the test temperatures in hydrogen. These results indicate a much higher rate of fuel loss from tests at 2500° C than those at 2200° C.

Heating and cooling rates. - The detrimental effects of thermal cycling W - 20-volume-percent UO_2 composites are somewhat decreased with increasing rates of heating and cooling during cycling, as shown in figure 4. However, the differences in the two curves are not as large as might be expected from the large differences in rates involved. Therefore, it appears that the test results are relatively insensitive to heating and cooling rates over the range investigated.

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Reference cyclic-test conditions. - Based on the results of the studies just shown and on the expected cycling conditions of the tungsten water-moderated reactor, a reference thermal-cycling test was established for further testing of W-UO_2 composites. The conditions for this test are summarized, as follows: test temperature range, ambient temperatures to 2500° C; test interval at 2500° C, 10 minutes; holding time between cycles at ambient temperatures, 10 minutes; heating and cooling rate, about 1000° C per minute; test atmosphere, purified hydrogen with a flow rate of 35 standard cubic feet per hour. These test conditions were used in most of the studies described in subsequent sections of this report.

Fuel loading. - The effect of fuel loading on fuel losses resulting from cycling W-UO_2 composites is shown in figure 5. The results show that fuel losses increase rapidly with fuel loading.

Methods of Reducing Effects of Thermal-Cyclic Fuel Losses

Additions of thorium dioxide to tungsten matrix. - Small additions (0.5 to 4 volume percent) of fine ThO_2 particles (0.58-μ diam) were added to the tungsten matrix in W-UO_2 composites by blending ThO_2, UO_2, and tungsten powders prior to pressing, sintering, and roll cladding. As is demonstrated in the fuel-loss data of figure 6, the rate of fuel loss from W - 20-volume-percent UO_2 composites during cycling decreased with increasing additions of ThO_2. The effect of a 4-volume-percent ThO_2 addition to a W - 20-volume-percent UO_2 composite is readily apparent in the photomicrographs of figure 7. The photomicrographs show more extensive fuel migration and loss, as well as grain boundary separation in the tungsten matrix and cladding, in one-half the number of cycles in the W - 20-volume-percent UO_2 composite (figs. 7(a) and (b)) compared with the W - 20-volume-percent - 4-volume-percent ThO_2 composite (figs. 7(c) and (d)). The photomicrographs of figures 7(c) and (d) show an additional phase (determined by electron microprobe analyses as being uranium-rich) within the UO_2 particles rather than at the W-UO_2 particle interfaces as had previously been observed in W - 20-volume-percent UO_2 composites without ThO_2 additions. The reason for this difference is not presently known.

Additional fuel-loss data showing the effect of a 2-volume-percent addition of ThO_2 on higher fuel loadings in W-UO_2 composites are shown in figure 8 (for the reference cycling conditions). These data indicate that small additions of ThO_2 are not as effective in prolonging the cyclic life of W-UO_2 composites at high fuel loadings.

Originally it was thought that the improved fuel-loss resistance of the W-UO_2 composites containing ThO_2 was primarily a result of both refinement and stabilization of the grain size of the tungsten matrix. As shown in the photomicrographs of figures 9

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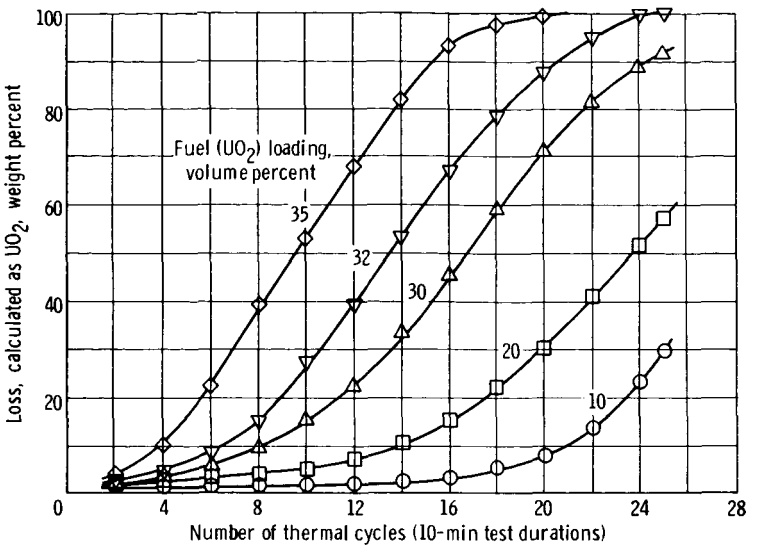

Figure 5. - Effect of fuel loading on thermal cycling of tungsten - uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

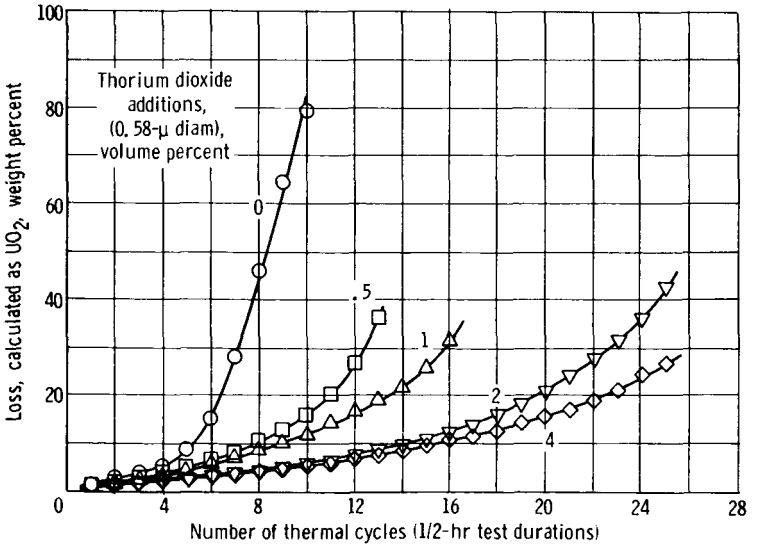

Figure 6. - Effect of thorium dioxide additions to tungsten in tungsten - 20-volume-percent uranium dioxide composites during thermal cycling. Composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

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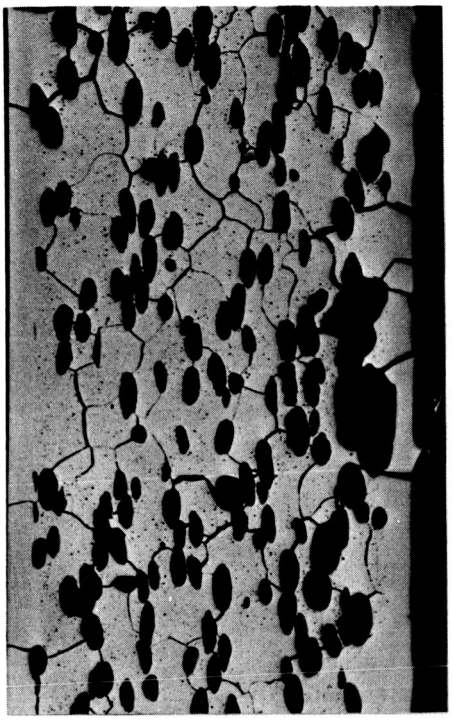
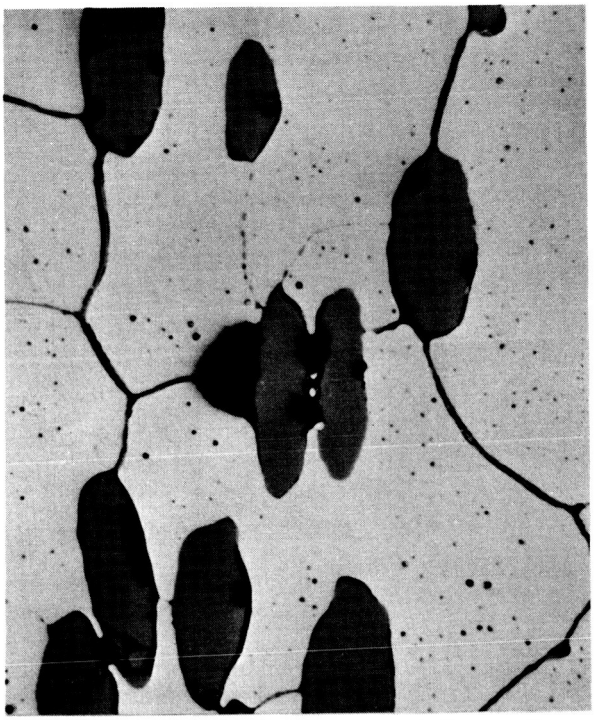
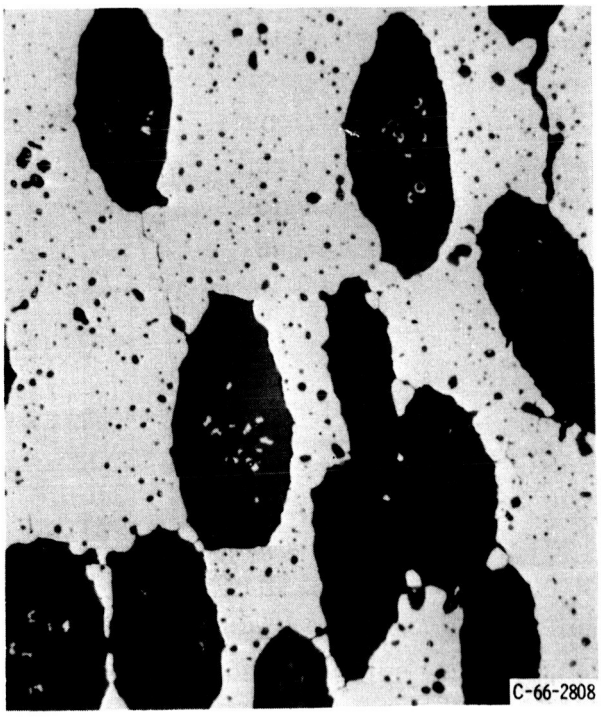


(a) Tungsten - 20-volume-percent uranium dioxide composite thermally cycled for six 1/2-hour durations. X100.



(b) Tungsten - 20-volume-percent uranium dioxide composite thermally cycled for six 1/2-hour durations. X500.

(c) Tungsten - 20-volume-percent uranium dioxide - 4-volume-percent thorium dioxide thermally cycled for twelve 1/2-hour durations. X100.



(d) Tungsten - 20-volume-percent uranium dioxide - 4-volume-percent thorium dioxide thermally cycled for twelve 1/2-hour durations. X500.

Figure 7. - Microstructures of tungsten - 20-volume-percent uranium dioxide composites thermally cycled at 2500° C in hydrogen showing effect of 4-volume-percent addition of thorium dioxide to tungsten matrix. Unetched.

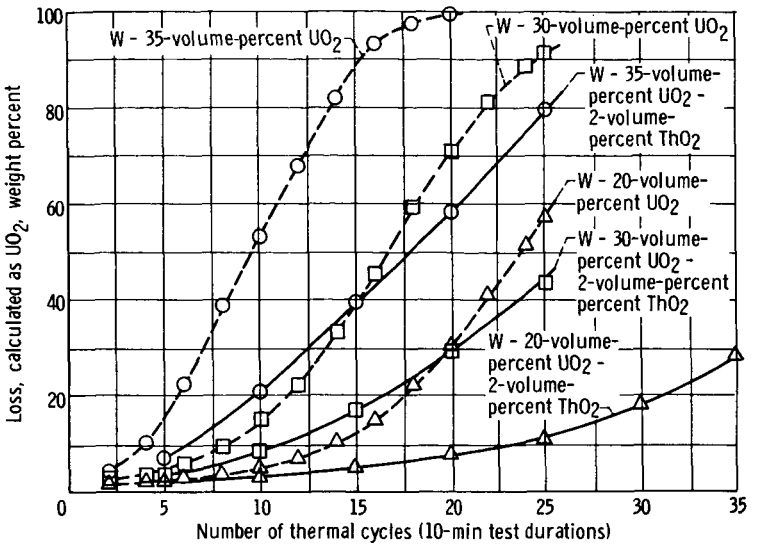
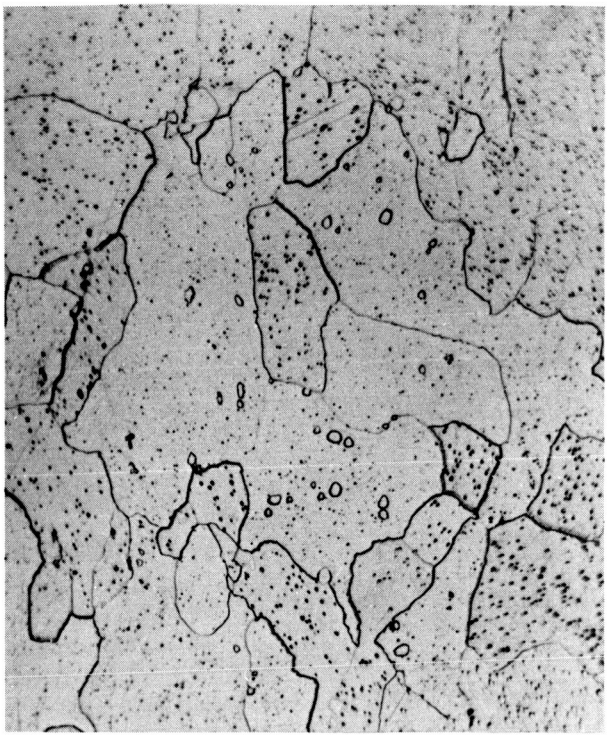
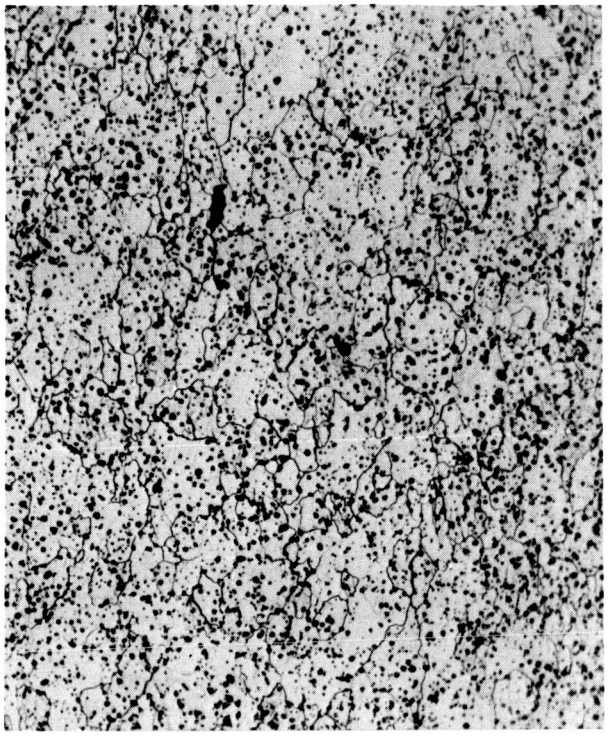


Figure 8. - Effect of 2-volume-percent addition of thorium dioxide to tungsten on fuel loading in tungsten - uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces); fuel particle size, about 50 microns.

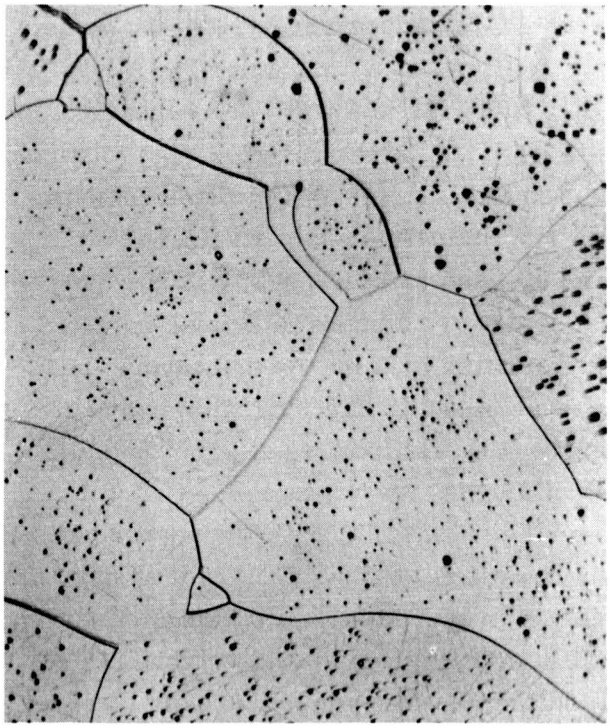
and 10, a 4-volume-percent addition of ThO_2 was very effective in refining the as-fabricated grain size in the tungsten composite (figs. 9(a) and (b)) and to a much lesser extent in the W - 20-volume-percent UO_2 composite (figs. 10(a) and (b)). The ultrafine grain structure in regions adjacent to the UO_2 particles in the W - 20-volume-percent UO_2 - 4-volume-percent ThO_2 composite (fig. 10(b)) is a result of high localized concentrations of ThO_2 particles that had restricted the grain growth in these regions. However, ThO_2 was not significantly effective in stabilizing the grain structure resulting from cycling to 2500° C for either tungsten (figs. 9(c) and (d)) or W - 20-volume-percent UO_2 (figs. 10(c) and (d)) composites. However, some preliminary data have indicated that small ThO_2 additions, if added to the tungsten matrix by a means that favors the formation of a much finer ThO_2 dispersion than is achieved by mechanical blending, greatly refine and stabilize the grain structure of W-UO_2 composites at 2500° C and further improve the resistance to fuel migration and loss. As an example, figure 11 (p. 16) shows photomicrographs of a W - 20-volume-percent UO_2 - 4-volume-percent ThO_2 composite that was tested for ten 1/2-hour durations at 2500° C in hydrogen. This composite was fabricated by using a powder that was prepared by mixing tungsten powders in an aqueous solution of thorium nitrate, followed by precipitating a thorium hydroxide gel on the tungsten powders with the addition of ammonium hydroxide, and then filtering and drying the precipitate. The total fuel loss for this composite was 3.5 weight percent UO_2 compared with 5.7 weight percent UO_2 for the similarly tested composite discussed previously (see fig. 6, p. 10). The fine grain structure of fig-



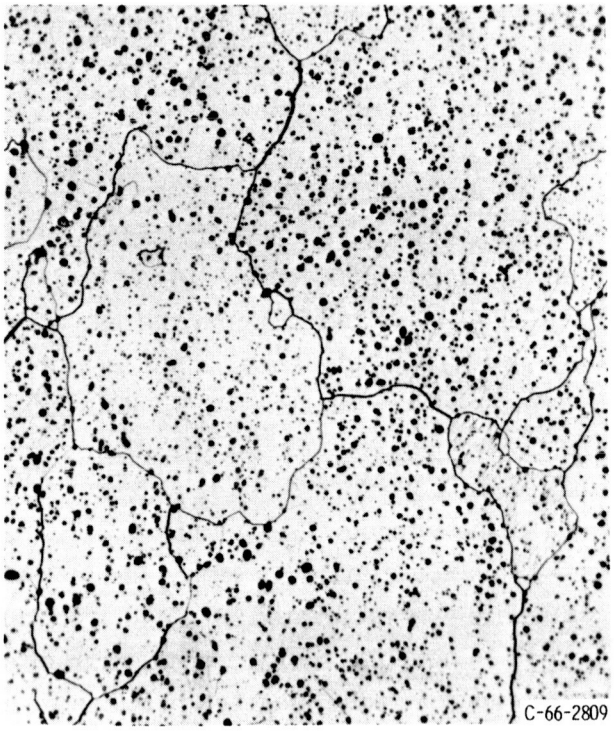
(a) Tungsten; noncycled (as-fabricated).



(b) Tungsten - 4-volume-percent thorium dioxide; noncycled (as-fabricated).



(c) Tungsten; thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen.



(d) Tungsten - 4-volume-percent thorium dioxide; thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen.

Figure 9. - Microstructures of tungsten and tungsten - 4-volume-percent thorium dioxide composites in noncycled and thermally cycled conditions. Etched. X250.

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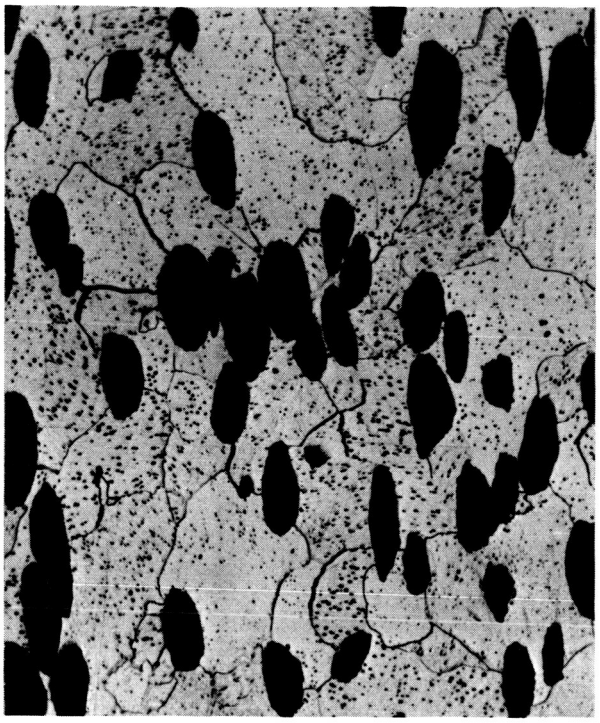
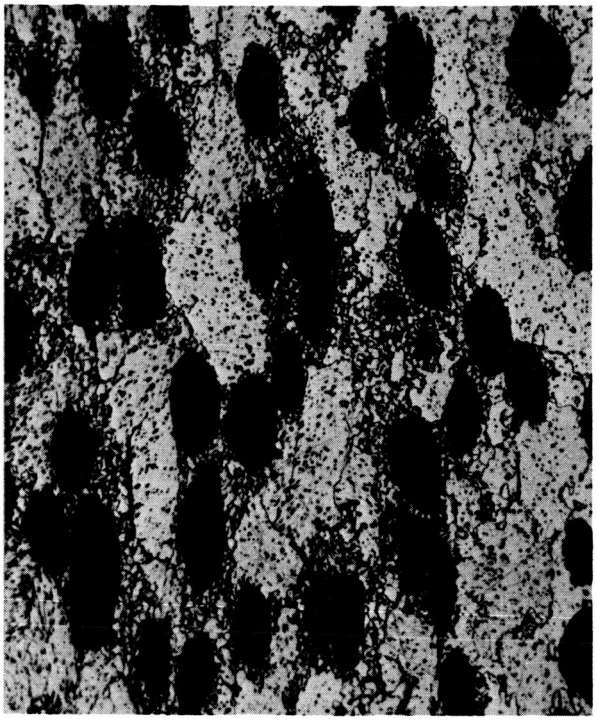
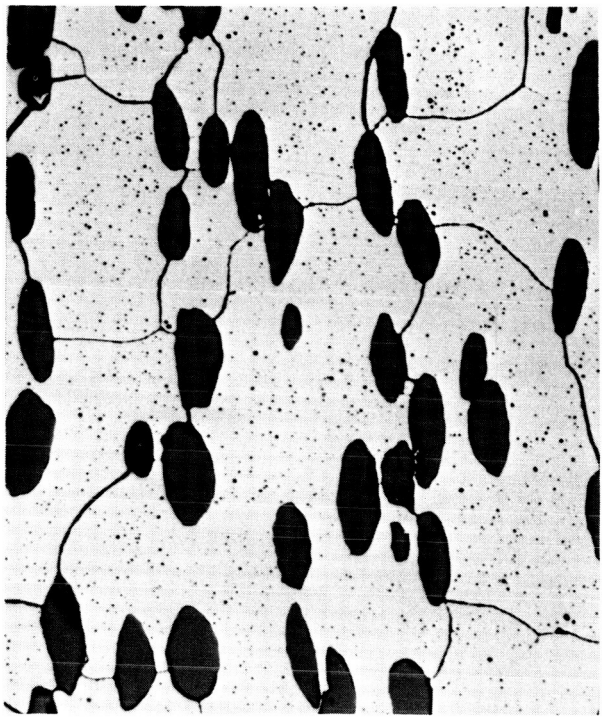


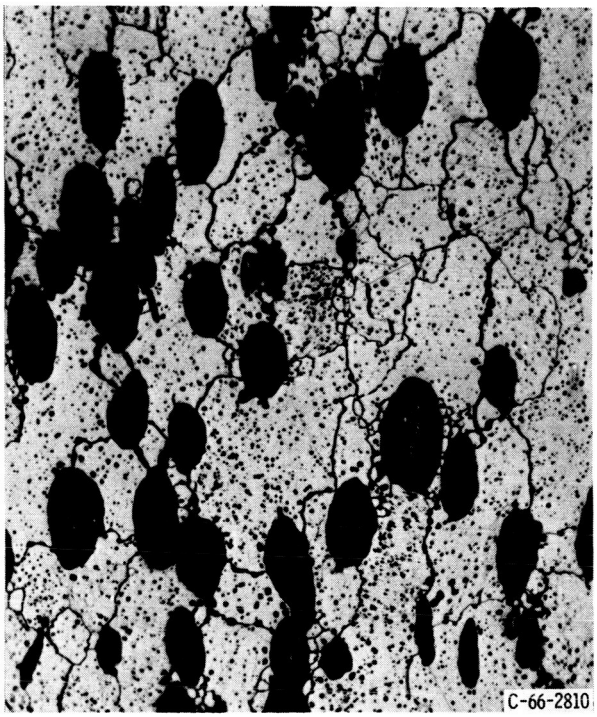
(a) Tungsten - 20-volume-percent uranium dioxide; noncycled (as fabricated).



(b) Tungsten - 20-volume-percent uranium dioxide - 4-volume-percent thorium dioxide; noncycled (as fabricated).



(c) Tungsten - 20-volume-percent uranium dioxide; thermally cycled for six 1/2-hour durations at 2500° C in hydrogen.



(d) Tungsten - 20-volume-percent uranium dioxide - 4-volume-percent thorium dioxide; thermally cycled for twelve 1/2-hour durations at 2500° C in hydrogen.

Figure 10. - Microstructures of tungsten - 20-volume-percent uranium dioxide composites in noncycled and thermally cycled conditions showing effects of 4-volume-percent addition of thorium dioxide to tungsten matrix. Etched. X250.

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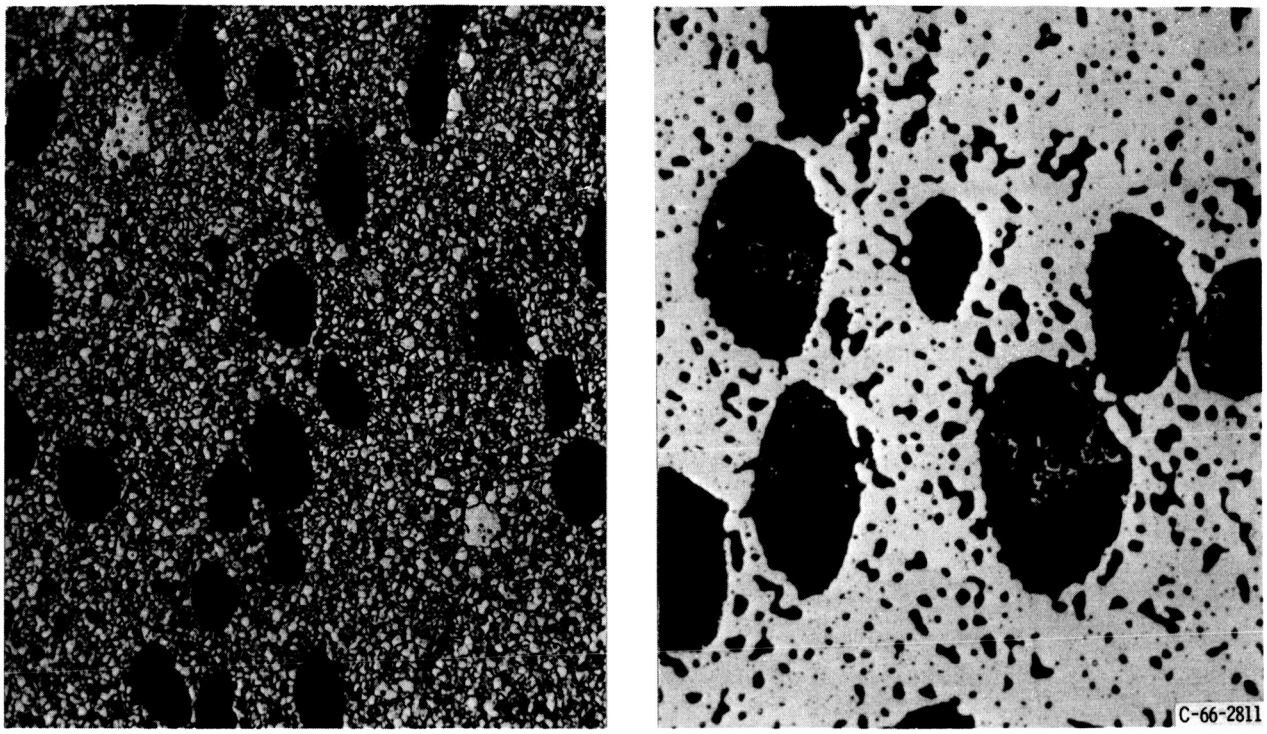

(a) Etched; X250. (b) Unetched; X500.

Figure 11. - Microstructures of thermally cycled tungsten - 20-volume-percent uranium dioxide - 4-volume-percent thorium dioxide composite after ten 1/2-hour durations at 2500° C in hydrogen. Composite was prepared from mixture of tungsten - thorium dioxide (precipitated) and uranium dioxide powders.

ure 11(a) and the apparent absence of fuel migration (fig. 11(b)) indicate that this structure also might be mechanically stronger than those shown in figures 7(c) and (d) and in figures 10(c) and (d).

Use of fine UO_2 particles. - In attempts to refine and also stabilize the grain size of the tungsten matrix, without the use of ThO_2 additions, fine (0.58 μ) UO_2 particles were used in place of the larger (50 μ) UO_2 microspheres. Comparison of the fuel losses from similarly cycled W - 20-volume-percent UO_2 composites containing the two UO_2 particle sizes is shown in figure 12. Typical microstructures of the composites containing the large UO_2 particles after 25 cycles are compared with those of the composites containing the fine UO_2 particles after 100 cycles in the photomicrographs of figures 13 and 14, respectively. The fuel-loss data (fig. 12) indicate that W - 20-volume-percent composites containing the fine UO_2 particles exhibit very good resistance to thermal-cyclic fuel losses. However, as yet it has not been possible to fabricate fully dense, crack-free composites of this type that contain fuel loadings greater than 30 volume percent by the present process.

The increase in the rate of fuel loss from composites containing the fine UO_2 particles (middle curve of fig. 12) is attributed to the development of submicroscopic

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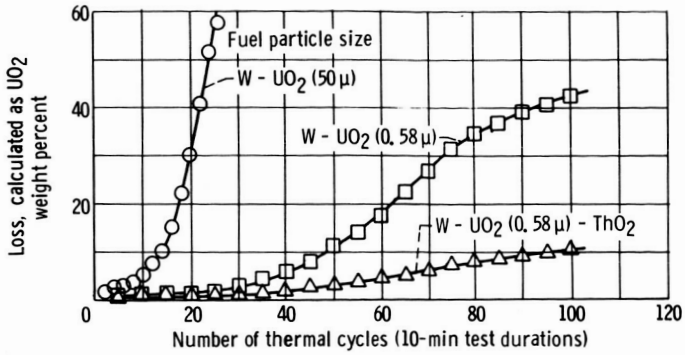
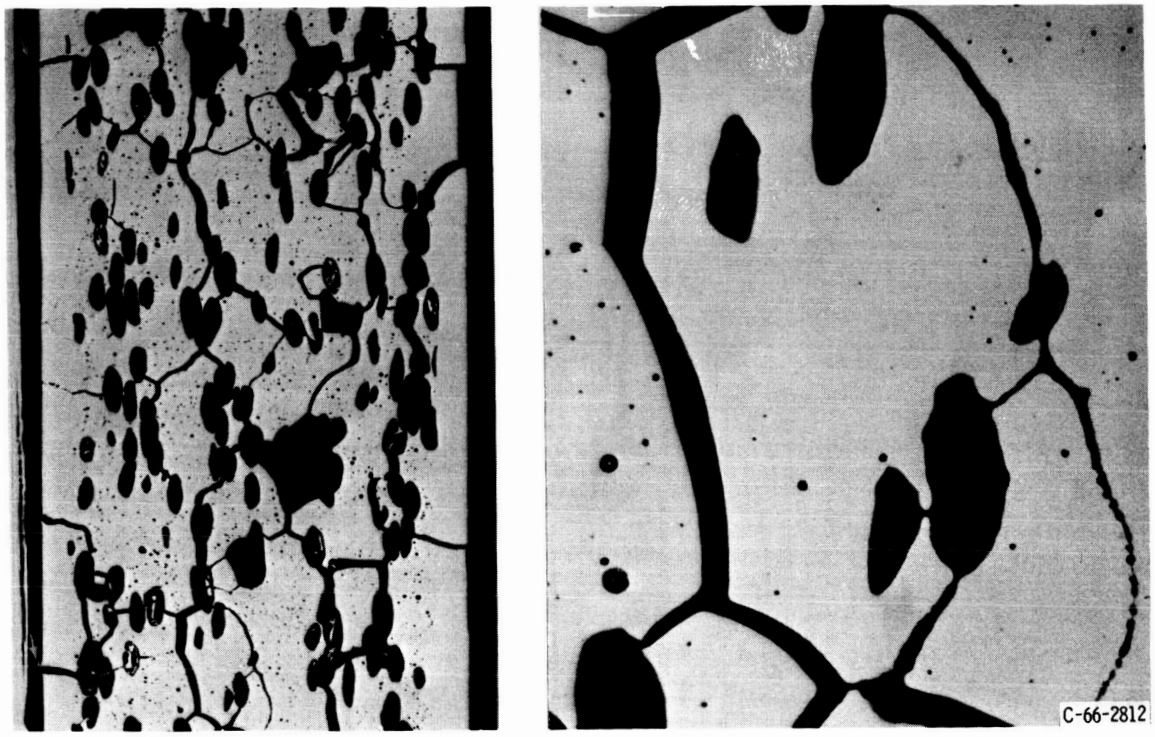


Figure 12. - Effects of fuel particle size and 2-volume-percent addition of thorium dioxide to tungsten on thermal-cyclic behavior of tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces).



(a) Arrows show tungsten tips on cladding surface. X100.

(b) X500.

Figure 13. - Microstructures of thermally cycled tungsten - 20-volume-percent uranium dioxide composite prepared with 50-micron-diameter particles of uranium dioxide. Composite was cycled for twenty-five 10-minute durations at 2500° C in hydrogen.

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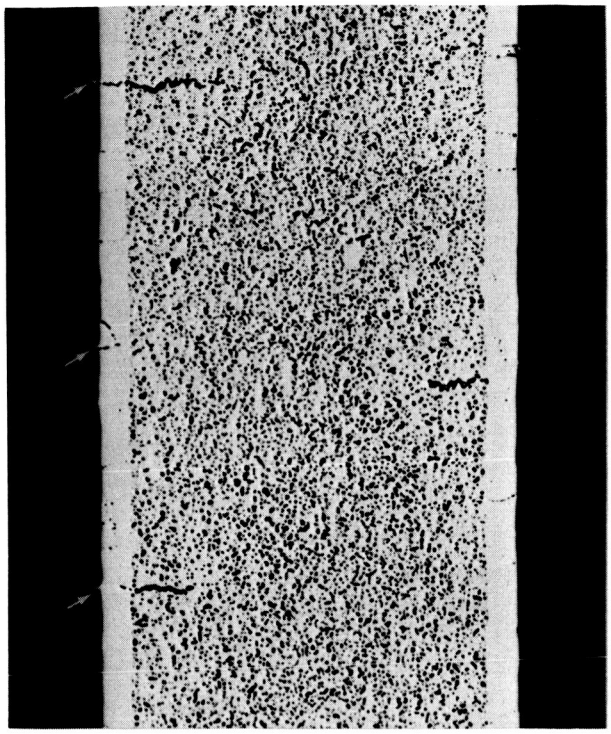
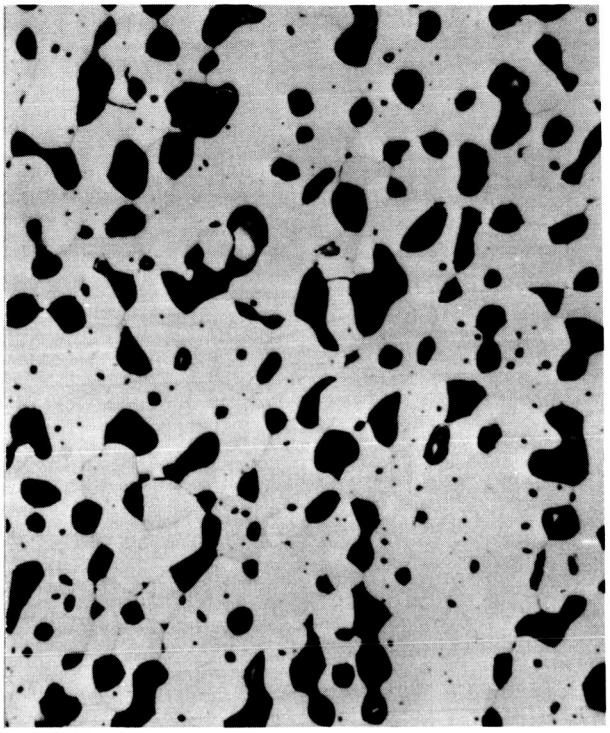
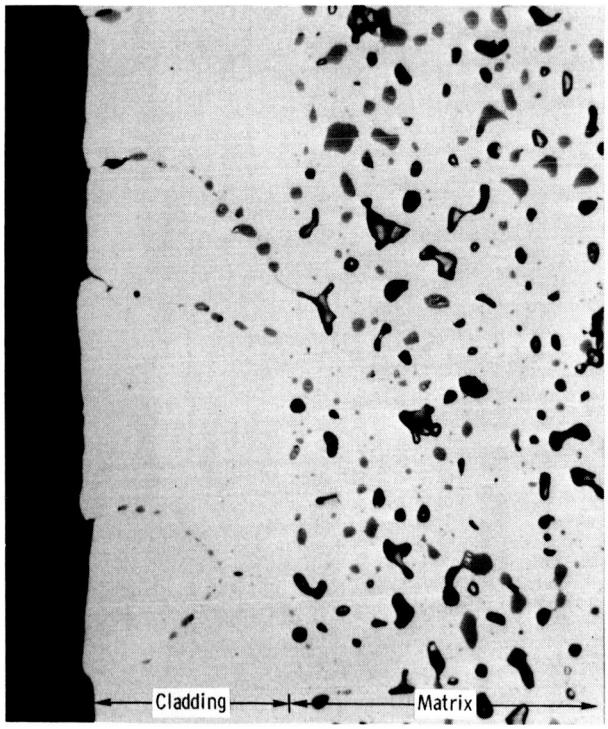


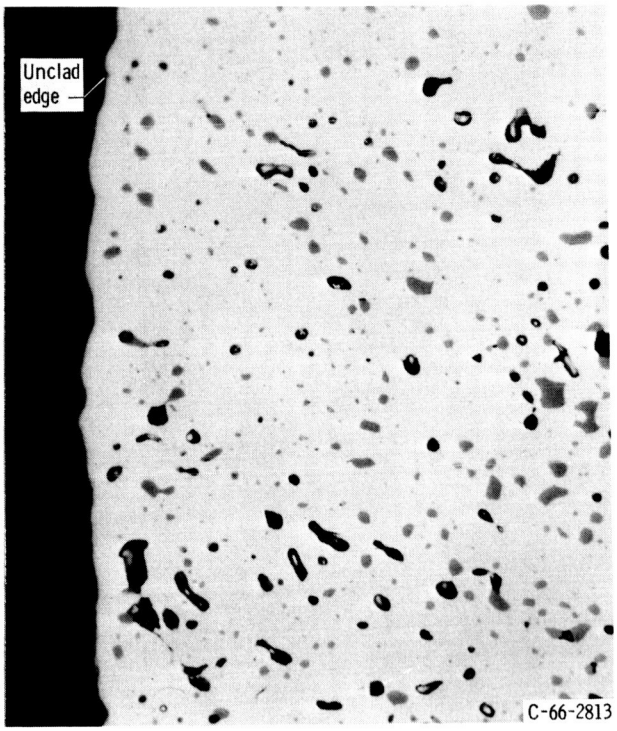
(a) Arrows show tungsten tips on cladding surface. X100.



(b) X1000.



(c) X500.



(d) X500.

Figure 14. - Microstructures of thermally cycled tungsten - 20-volume-percent uranium dioxide prepared with 0.58-micron-diameter particles of uranium dioxide. Composite cycled for one hundred 10-minute durations of 2500° C in hydrogen. Unetched.

fissures during fabrication that propagate and enlarge during thermal cycling, as shown in the photomicrograph of figure 14(a). Since the as-received 0.58-micron UO_2 powder was highly hyperstoichiometric (O/U = 2.14), it is possible that high internal gas pressures were generated during sintering that led to the formation of these fissures. The photomicrographs of figure 13 show considerable fuel migration and grain boundary separation in both the matrix and cladding of the composite containing the large UO_2 particles; however, such migration and separation is not evident in the matrix of the composite containing the fine UO_2 particles (fig. 14(b)). Fuel migration in this latter composite, however, is definitely apparent in the large grain structure of the tungsten cladding in the photomicrograph of figure 14(c) (which shows a typical area of the core-to-clad interface). However, the presence of the UO_2 particles in proximity to the unclad edge, as shown in the photomicrograph of figure 14(d), indicates the high resistance to thermal-cyclic fuel loss in a core of this type of composite.

An interesting observation that has been noted many times in the course of these studies is evident in the photomicrographs of figures 13 and 14(a) and (b) This is the appearance of tungsten tips (indicated by the arrows) on the cladding on both sides of the grain boundaries through which the fuel has migrated. It is suggested that this may be a result of mass transport of tungsten by uranium, because tungsten is slightly soluble in either liquid or solid uranium at elevated temperatures (ref. 13), and/or by tungsten oxides (or tungsten-uranium oxides).

The use of fine UO_2 particles in place of the larger UO_2 microspheres did indeed refine and somewhat stabilize the grain size of the tungsten matrix as is shown in the photomicrographs of figure 15. The microstructures in figure 15(b) and (d) are those of the thermally cycled composites shown in figures 13 and 14 after etching. Evidence of fuel migration is not readily apparent in the tungsten matrix of the thermally cycled composite containing the fine UO_2 particles (fig. 14) because of the fine grain structure of the matrix (fig. 15(d)).

Attempts were made to determine if the high resistance to thermal-cyclic fuel losses of composites containing the fine UO_2 particles could be further improved with the use of ThO_2 additions to the tungsten matrix. As shown in figure 12, a further improvement in fuel retention was obtained. The reasons for the added improvement are apparent in comparing the photomicrographs of the figures 14(a) and (b) and 15(c) and (d) with those in figure 16, which shows the microstructures of a similarly fueled and tested composite but containing a 2-volume-percent addition of ThO_2. The area containing the greatest concentration of fissures observed in a W - 20-volume-percent UO_2 - 2-volume-percent ThO_2 composite after cycling is shown in cross section in the photomicrograph in figure 16(a). Comparison of these photomicrographs indicates that in the composite containing the ThO_2 addition, (1) a smaller amount of fuel is present in the large grain structure of the tungsten cladding (figs. 14(a) and 16(a)), (2) less propagation and en-

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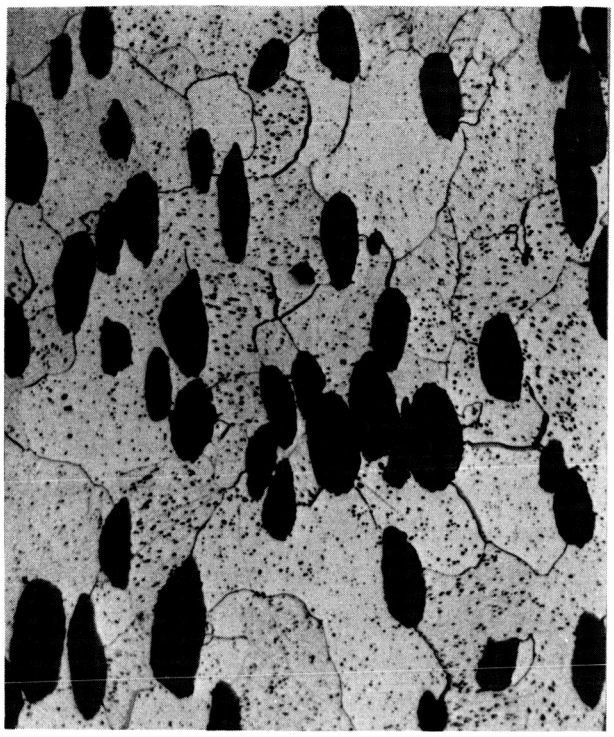
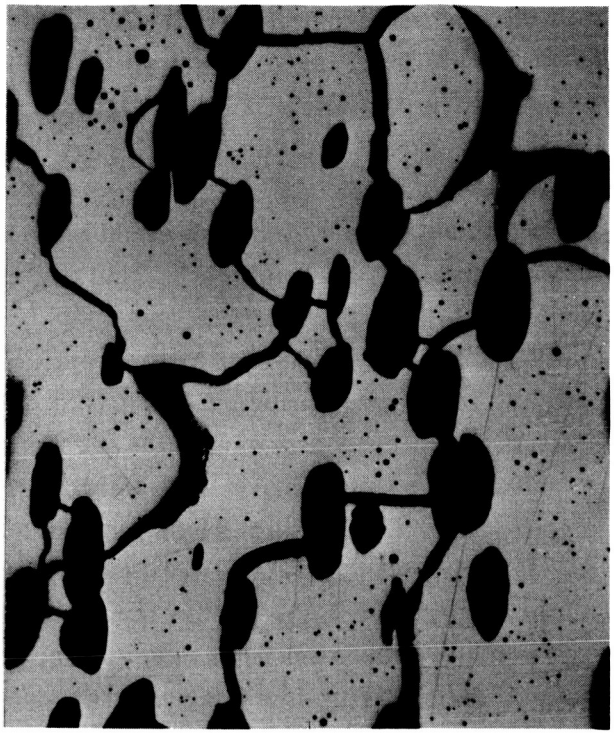
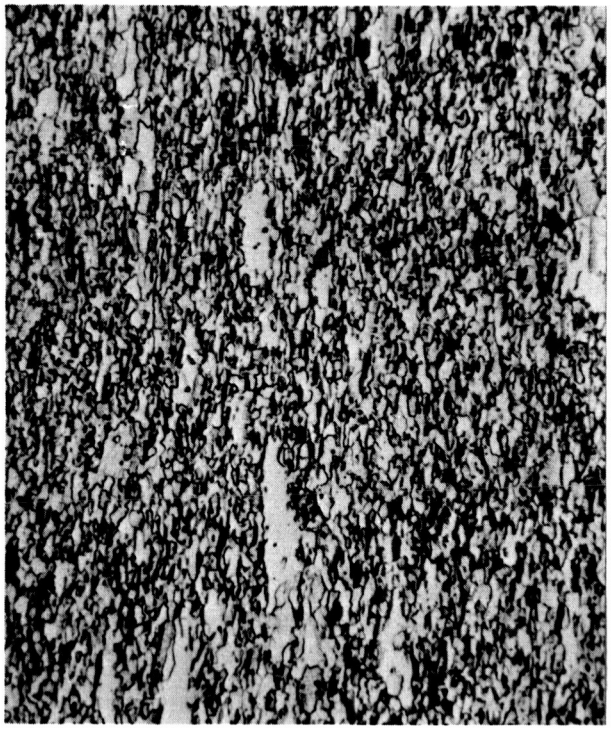


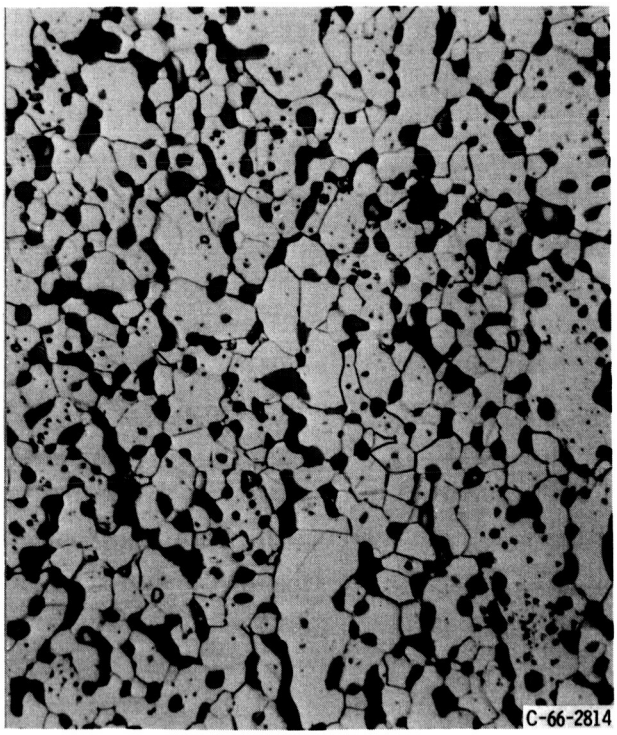
(a) Noncycled (as-fabricated); uranium dioxide particle size, 50 microns; average grain diameter, 0.064 millimeter. X250.



(b) Thermally cycled; uranium dioxide particle size, 50 microns; average grain diameter, 0.172 millimeter. X250.



(c) Noncycled (as-fabricated); uranium dioxide particle size, 0.58 micron; average grain diameter, 0.006 millimeter. X500.



(d) Thermally cycled; uranium dioxide particle size, 0.58 micron; average grain diameter, 0.018 millimeter. X500.

Figure 15. - Microstructures of tungsten - 20-volume-percent uranium dioxide composites in noncycled and thermally cycled conditions showing effect of uranium dioxide particle size. Etched. (Parts (b) and (d) are microstructures of composites shown in figs. 13 and 14 after etching.)

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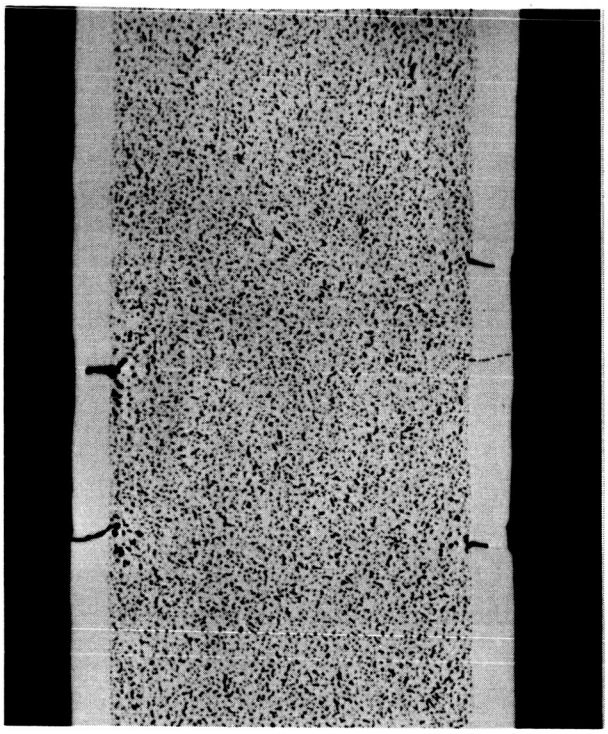
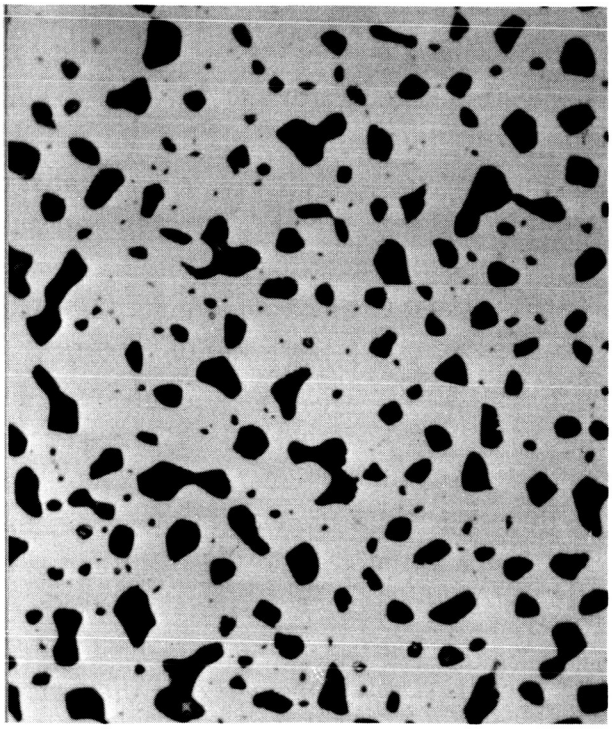
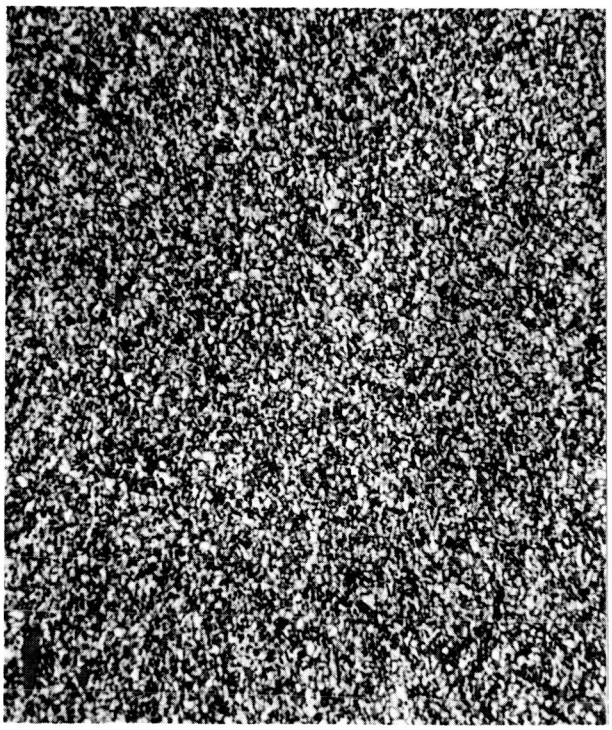


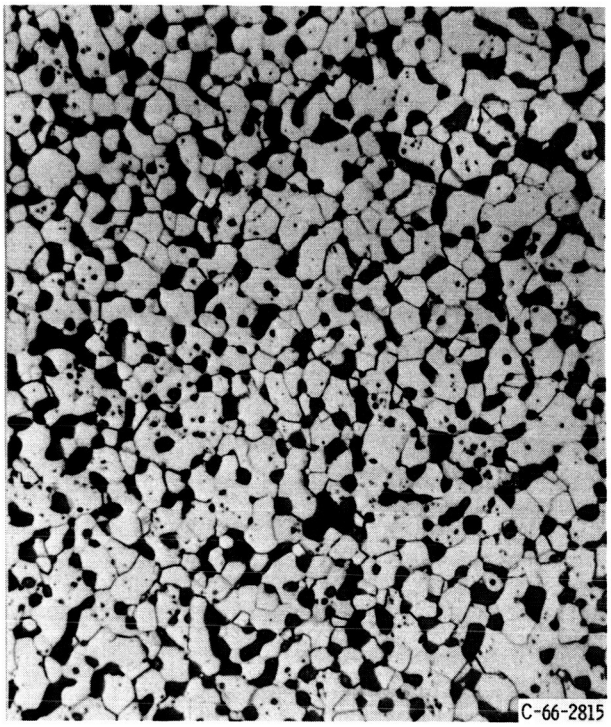
(a) Thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen; unetched; X100.



(b) Thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen; unetched; X1000.



(c) Noncycled (as-fabricated); etched; X500; average grain diameter, 0.002 millimeter.



(d) Thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen; etched; X500; average grain diameter, 0.010 millimeter.

Figure 16. - Microstructures of tungsten - 20-volume-percent uranium dioxide - 2-volume-percent thorium dioxide composites showing effect of fine (0.58 μ) uranium dioxide particles.

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largement of fissures has occurred (figs. 14(a) and 16(a)), and (3) a finer grain structure of the tungsten matrix has been maintained in both the as-fabricated and thermally cycled composites (figs. 15(c) and (d) and 16(c) and (d)). The extent of fuel coalescence appears to be about the same in both composites after cycling (figs. 15(c) and (d) and 16(d)). It is, however, extremely difficult to distinguish UO_2 from ThO_2 because of the similarity of the metallographic characteristics of these two oxides.

Metal-oxide additions to fuel. - Results of a study reported in reference 3 have shown that additions of other metal oxides (nominally 10 mole percent of either ThO_2, CaO, or ZrO_2) in solid solution with UO_2 greatly inhibit the rate of fuel loss from W - 20-volume-percent UO_2 composites during thermal cycling. In that study, composites with and without a 2-volume-percent addition of ThO_2 to the tungsten matrix were tested for 10-minute durations at 2500° C in hydrogen. Although each oxide addition to the UO_2 decreased the rate of fuel loss, the effect was most pronounced for the composites containing CaO in the UO_2, and more so, for composites containing additional ThO_2 in the matrix. Metallographic observations of the composites containing CaO after testing confirmed the improved stability of these composites, that is, very little fuel migration was observed. In the following discussion and figures, W - 20-volume-percent UO_2 composites in which the UO_2 contains a 10-mole-percent addition of a metal oxide (M_aO_b) will be designated as W-UO_2:M_aO_b and those with additional ThO_2, W-UO_2:M_aO_b-ThO_2.

Recent results of thermal cycling tests on W-UO_2:CaO composites are shown in figure 17. For comparison, the results of the previously discussed methods of reducing fuel losses are also shown in this figure. It is apparent from these data that the CaO additions are quite effective in prolonging the cyclic life of the W-UO_2 composites. As can be seen, the composites with either fine UO_2 or large UO_2:CaO particles held up relatively well (less than 10-weight-percent fuel loss) for at least 25 cycles, but similar composites with ThO_2 in the matrix held up as well for 85 cycles (14.2 hr total at 2500° C). Based on these results, composites with fine UO_2:CaO fuel plus ThO_2 in the matrix might be expected to exhibit even lower rates of fuel loss. However, very recent results (reported in ref. 14) have indicated that a 10-mole-percent addition of yttrium oxide (Y_2O_3) to the UO_2 is more successful in improving the stability to thermal-cyclic fuel losses from W - 35-volume-percent UO_2 composites than is CaO at the same concentration in the UO_2.

The preceding results were for composites that were partly clad; that is, only the two major surfaces were clad with tungsten and the edges were unclad. As shown in the results presented in the appendix on the effect of cladding, complete cladding of W-UO_2 composites is required in order to minimize thermal-cyclic fuel losses. Therefore, as an additional comparison of the three methods of reducing thermal-cyclic fuel losses, the behavior of completely clad W - 20-volume-percent UO_2 composites is shown in figure 18. These data indicate that excellent fuel retention characteristics (less than

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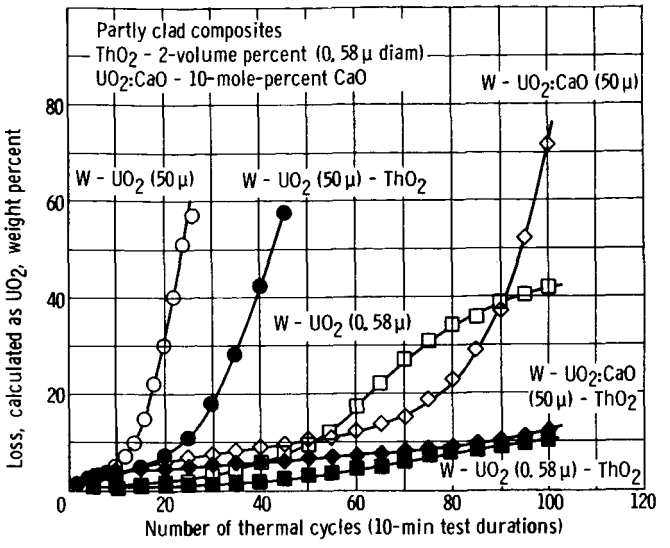

Figure 17. - Effect of thermal cycling on various partly clad tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, $1\frac{3}{8}$ by 1 by 0.021 inch (approximately 0.002 in. tungsten cladding on major surfaces). Approximate fuel particle size indicated in parenthesis.

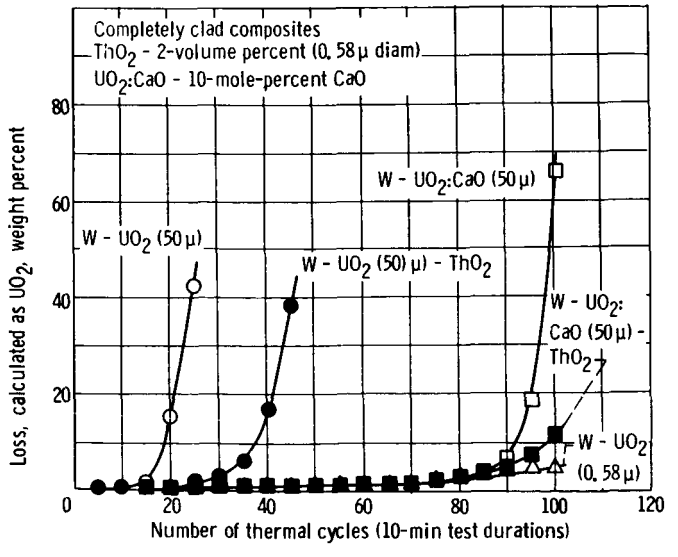

Figure 18. - Effect of complete cladding on fuel loss resulting from tungsten - 20-volume-percent uranium dioxide composites during thermal cycling. Composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Composite size, about $1\frac{1}{4}$ by $\frac{5}{8}$ by 0.021 inch (approximately 0.002 and 0.2 in. tungsten cladding on major surfaces and edges, respectively); approximate fuel particle size indicated in parenthesis.

1-weight-percent fuel loss in 25 cycles) were obtained with completely clad composites containing either large UO_2:CaO particles or fine UO_2 particles. However, at least a 2-volume-percent addition of ThO_2 to the tungsten matrix would be required in composites containing large UO_2:CaO particles in order that the fuel loss for these composites would be less than 10-weight percent in 95 cycles. The results reported in reference 14, however, also indicate that completely clad W-UO_2:Y_2O_3 composites have better fuel retention properties than completely clad W-UO_2:CaO composites.

DISCUSSION

The causes of accelerated fuel losses from W-UO_2 composites under thermal-cycling conditions have been stated in reference 2. The basic cause appears to be a partial decomposition of UO_2 at elevated temperatures with loss of oxygen to the tungsten matrix. On cooling, the oxygen-deficient UO_2 (hereinafter referred to as UO_{2-x}) disproportionates into uranium metal and UO_2. During successive heating and cooling cycles, the uranium metal, which has a low melting point of 1130° C, migrates along the tungsten grain boundaries. This migration causes grain boundary separation in the composites and rapid loss of fuel by vaporization. Furthermore, it

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appears that the large differences in the thermal expansivities of UO_2, tungsten, and uranium may cause enhanced migration of uranium metal and also promote grain boundary separation during thermal cycling.

Effect of Test Variables on Thermal-Cyclic Fuel Losses From Tungsten - Uranium Dioxide Composites

Atmosphere. - The fuel-loss data obtained in the initial study (ref. 2) showed that the losses from W-UO_2 composites during thermal cycling were considerably higher in hydrogen than in either helium or vacuum. In that study, the composites were cycled between ambient temperatures (about 20° C) and 2500° C in each of the three atmospheres. Based on these initial data, it was proposed that the presence of a hydrogen atmosphere at high temperatures apparently accelerates the decomposition of UO_2 by combining with the oxygen being released. However, as shown in the results of figure 2 (p. 8) herein (comparison of fuel losses represented by curves A and B), the rate of fuel loss in hydrogen was substantially reduced when composites were heated and cooled in helium below 1100° C. This would indicate that uranium hydride (UH_3) formation, which occurs at temperatures below 300° C (ref. 15) was prevented or at least minimized in the composites that were cycled in hydrogen to 2500° C, but heated and cooled in helium below 1100° C. The formation of the hydride from metallic uranium is accompanied by complete disintegration of the metal to powder (ref. 15). This disintegration is the result of a large volume change accompanying the formation of UH_3 (ref. 16). In addition, hydriding at low temperatures followed by reheating (as in thermal cycling) may cause catastrophic pressure buildups because of the high dissociation pressures of UH_3; the dissociation pressure reaches 1 atmosphere at about 430° C. The eventual failure of the composites when cycled exclusively in hydrogen (curve A of fig. 2) is, therefore, believed to be a result both of decomposition of the UO_2 at elevated temperatures and of UH_3 formation at low temperatures. It is possible that some hydrogen could have been present during the low-temperature treatments in helium (curve B of fig. 2) as a result of incomplete displacement in the available time or of absorption of hydrogen in the tungsten or the furnace lining. If this was true, the fuel losses of curve B are not truly representative of the intended cycling conditions; the fuel losses would be smaller if no hydrogen was present at low temperatures.

As is also shown in the results of figure 2, high-temperature treatments in helium with low-temperature treatments in hydrogen (curve C) resulted in the lowest rate of fuel loss until the termination of testing, that is, 15 thermal cycles. A low rate of fuel loss would be expected if decomposition of UO_2 is minimal, because the effect of UH_3

formation on fuel loss would then be minimal. However, it is felt that additional testing eventually would cause sufficient decomposition of UO_2 to occur so that the effect of UH_3 formation would then be observed.

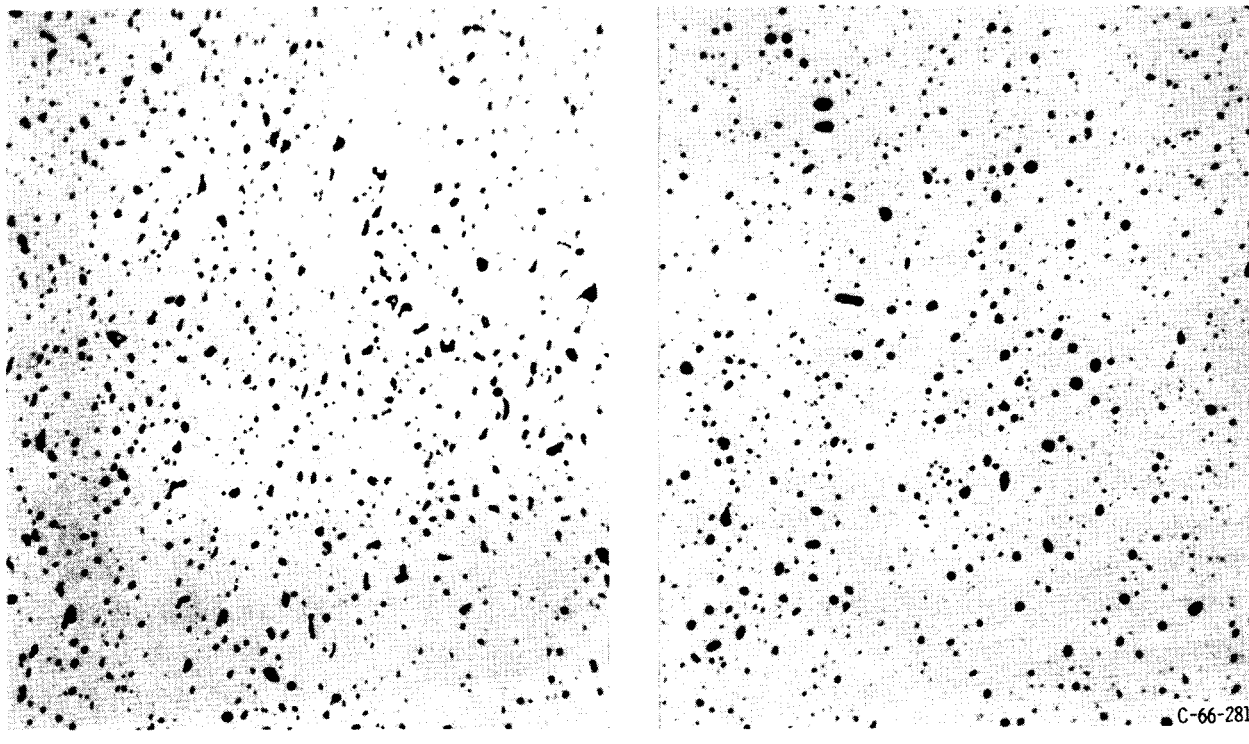
Temperature. - The lower rate of fuel loss resulting from thermal cycling in hydrogen to 2200° C, rather than to 2500° C (fig. 3, p. 9), is probably a result primarily of lower rates of decomposition of UO_2 and migration and vaporization of the decomposition and reaction products (uranium species, oxygen, water vapor, etc.) at the lower temperature. The results shown in figure 3 indicate that thermal cycling would probably not be a serious problem if the reactor operated at temperatures below 2200° C (at least for the operating times indicated in these tests).

Fuel loading. - The increase in fuel losses with increased fuel loading (fig. 5, p. 10) is presumably caused primarily by (1) a larger amount of UO_2 being decomposed at the test temperature, and (2) a decrease in the interparticle spacing that increases the probability of interconnection of fuel particles. The latter factor would decrease the transport time required for migration and vaporization of the decomposition and reaction products. Also, since the interparticle spacing decreases with increasing fuel loading, the stresses due to the large difference in the thermal expansivities of tungsten and UO_2 may increase and thus result in an increase in the rate of fuel loss.

Methods of Reducing Effects of Thermal-Cyclic Fuel Losses

Additions of thorium dioxide to tungsten matrix. - The improved fuel-loss resistance of W-UO_2 composites containing ThO_2 in the tungsten matrix may be explained by one or both of the following hypotheses: (1) ThO_2 forms solid solutions with UO_2 (ref. 17), and/or (2) ThO_2 increases the internal surface area (grain boundaries plus phase interfaces) of the composites.

In regard to the first hypothesis, as the fuel migrates along the tungsten grain boundaries, it may interact with the ThO_2 particles and form solid solutions that have higher melting points and greater stability than the fuel. Several investigators (refs. 3 and 18) have shown that in either static or cyclic tests at temperatures of 2500° C and above in hydrogen, solid solutions of ThO_2 and UO_2 in W-UO_2:ThO_2 composites have lower rates of fuel loss than W-UO_2 composites containing the same fuel loading. In regard to the second hypothesis, since ThO_2 particles of the size used in this study are highly stable at elevated temperatures in tungsten, even under thermal-cyclic testing, as is shown in the photomicrographs of figure 19, the internal surface area of the W-UO_2 composites is increased and maintained with ThO_2 additions. Catastrophic interactions between UO_2 and impurities (which may result in the formation of gaseous products that have high vapor pressures, low melting eutectics, etc.) could be reduced because



(a) Noncycled (as-fabricated).

(b) Thermally cycled for one hundred 10-minute durations at 2500° C in hydrogen.

Figure 19. - Microstructures of unfueled tungsten - 4-volume-percent thorium dioxide composites in noncycled and thermally cycled conditions. Unetched. X500.

impurity concentrations per unit area would decrease with an increase in the internal surface area of the composites. As an example, tungsten oxides that may be present in the grain boundaries are known to form eutectics with UO_2 that have melting points as low as 1300° C and probably lower (ref. 19).

Use of fine uranium dioxide particles. - The high resistance to thermal-cyclic fuel losses for W-UO_2 composites containing the fine UO_2 particles is believed to be a result primarily of the fine grain structure of the tungsten matrix. Since the fuel migrates along the grain boundaries of the matrix, a decrease in the grain size would increase the distance for fuel migration and, therefore, would increase the transport time required for subsequent fuel loss through vaporization at the surfaces of the composites. Also, since the internal surface area of the composite increases with a decrease in the grain size, catastrophic interactions between UO_2 and impurities could be reduced with the use of fine UO_2 particles in the W-UO_2 composites.

Metal-oxide additions to fuel. - The improved stability of W-UO_2:CaO and W-UO_2:Y_2O_3 composites, as discussed in detail in references 3 and 14, respectively, is thought to be a result primarily of oxygen vacancies that can be introduced into the UO_2 fluorite structure at elevated temperatures by the presence of either calcium or yttrium ions without the possible formation of uranium metal at lower temperatures.

The rate of decomposition of UO_2 is believed to be reduced as a result of the formation of a defect UO_2 structure.

SUMMARY OF RESULTS

The effects of some test and material variables on the thermal-cyclic fuel losses from tungsten-clad tungsten - uranium dioxide composites were studied as part of the NASA water-moderated, thermal-reactor program. For most of these studies, tungsten - 20-volume-percent uranium dioxide composites that consisted of partly clad rectangular plates (major surfaces clad with the edges unclad) were subjected to thermal cycles between ambient temperatures and 2500° C in a flowing hydrogen atmosphere at atmospheric pressure. Significant results of these studies are summarized as follows:

1. The rate of fuel loss (weight percent fuel loss per cycle) was shown to be accelerated more by cycling exclusively in hydrogen than in duplex-atmosphere environments (i.e., use of either hydrogen or helium within various temperature ranges).
2. The rate of fuel loss increased rapidly with an increase in the maximum cycling temperature, that is, from 2200° to 2500° C.
3. Fuel losses increased rapidly with increases in fuel loading.

The high rates of fuel loss associated with cycling tungsten - uranium dioxide composites in hydrogen were substantially reduced by three methods, which are, in the order of increasing effectiveness,

1. Small additions of fine (less than 1 μ) thorium dioxide particles to the tungsten matrix
2. Use of fine (less than 1 μ) uranium dioxide fuel particles instead of large (50 μ) fuel particles
3. Additions of metal oxides in solid solution with uranium dioxide

Complete cladding of tungsten-uranium dioxide composites is required in order to minimize thermal-cyclic fuel losses. For example, the fuel losses of completely clad composites containing either fine uranium dioxide or large uranium dioxide:calcium oxide (about 50 μ) particles were less than 1 weight percent in 25 cycles compared with as much as about 10 weight percent for similar but partly clad composites.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 24, 1966,
122-28-01-01-22.

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APPENDIX - PRELIMINARY STUDY OF EFFECT OF CLADDING ON REDUCING THERMAL-CYCLIC FUEL LOSSES FROM TUNGSTEN - URANIUM DIOXIDE COMPOSITES

Cladding of W-UO_2 composites was shown in reference 2 to be required in order to prevent fuel losses due to vaporization of surface and interconnected fuel particles. Since thermal-cyclic fuel losses are a consequence of fuel vaporization, some data have been obtained on the effect of cladding on reducing these losses.

A series of partly clad composites of equal thickness (i. e., both core and cladding), but of different sizes, were cycled to 2500° C in hydrogen in order to determine the effect of composite size and, indirectly, the effect of cladding on the thermal-cyclic fuel losses from W - 20-volume-percent UO_2 composites containing UO_2:CaO. The fuel-loss data for composites of three different sizes are presented in figure 20. The initial fuel losses of composites A, B, and C are considered to be a result of vaporization of the surface and interconnected fuel particles at the unclad edges of the composites. As shown in figure 20, each composite size had a different clad-to-unclad surface-area ratio C/U. As is readily apparent, both the initial fuel loss and the rate of fuel loss decrease with increasing C/U ratio of the composite. In addition, the cyclic life (i. e., the number of thermal cycles at the onset of catastrophic rates of fuel loss) of the com-

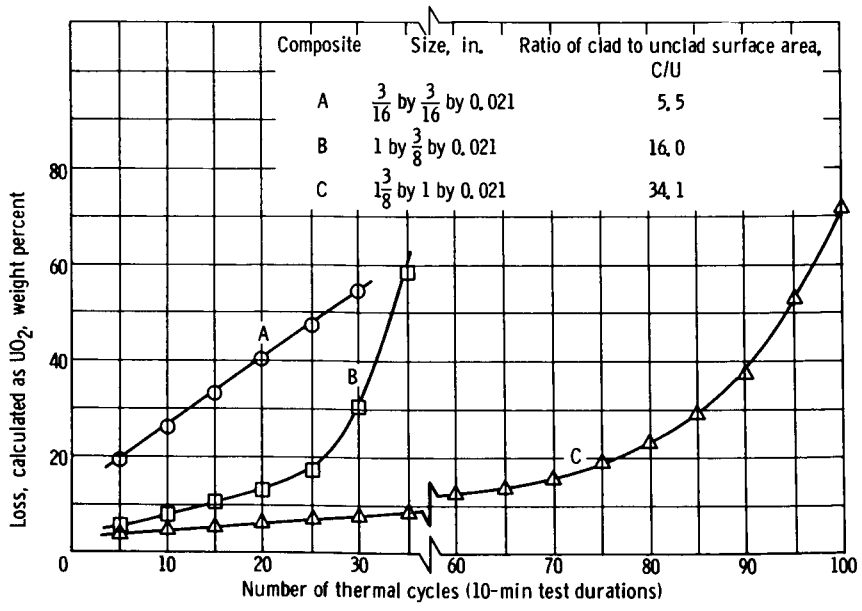

Figure 20. - Effect of composite size on thermal-cyclic behavior of partly clad tungsten - 20-volume-percent uranium dioxide:calcium oxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Approximately 0.002 inch tungsten cladding on major surfaces; fuel particle size, about 50 microns.

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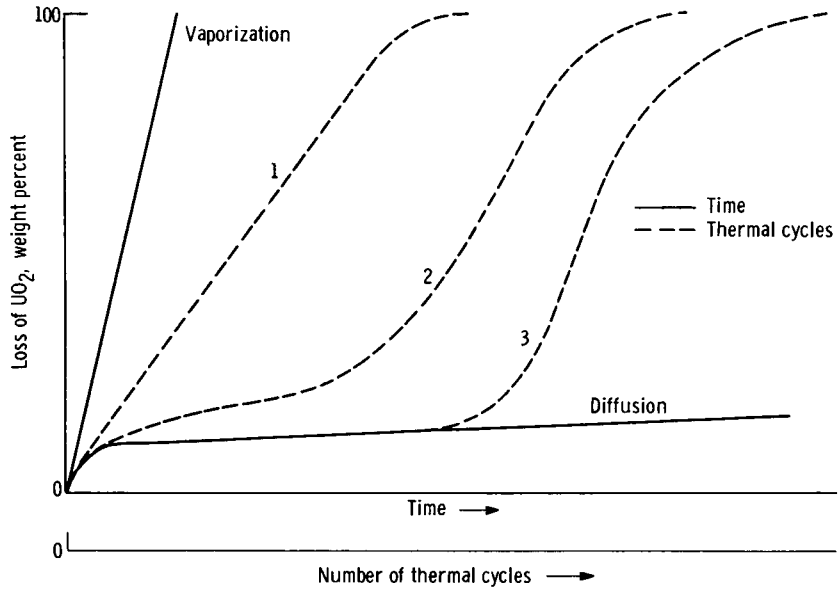

Figure 21. - Schematic representation of fuel losses from partly clad tungsten-uranium dioxide composites as function of time and number of thermal cycles of constant temperature and pressure.

posite correspondingly increases with the C/U ratio. For discussion purposes, figure 21 schematically represents the extreme as well as intermediate rates of fuel loss from partly clad W-UO_2 composites at constant temperature (and pressure). The rates of fuel loss represented in figure 21 can be considered as percent fuel loss per cycle since each cycle directly involves time at temperature. The upper linear curve (due solely to vaporization losses) would not be, and has been shown not to be, the behavior of W-UO_2 composites during the early stage of cycling. The lower curve due to initial vaporization losses followed by diffusion (migration) losses as a result of vaporization at the free surfaces would hopefully be expected of W-UO_2 composites during cycling. Fuel losses represented by this curve, however, have been obtained only for partly clad W-UO_2 composites that were statically tested at elevated temperatures, that is, without intermittent cooling to ambient temperatures (ref. 2). Curves 2 and 3 (superimposed in fig. 21), which are typical of the thermal-cyclic behavior of W-UO_2 composites, are believed to be a result of thermal decomposition of UO_2 at elevated temperatures, disproportionation of UO_{2-x} at intermediate temperatures, and UH_3 formation at lower temperatures. The onset of catastrophic rates of fuel loss (cyclic life) is caused primarily by tungsten grains being enveloped with fuel. This results in fuel losses that are predominantly a result of vaporization rather than diffusion through the tungsten grain boundaries. Curve 1 would be expected of W-UO_2 composites during cycling in which vaporization is the predominate mode of fuel loss. Since curves 1, 2, and 3 are somewhat similar to those of composites A, B, and C, respectively, in figure 20, it is believed that an increase in the C/U ratio would increase the transport time required for

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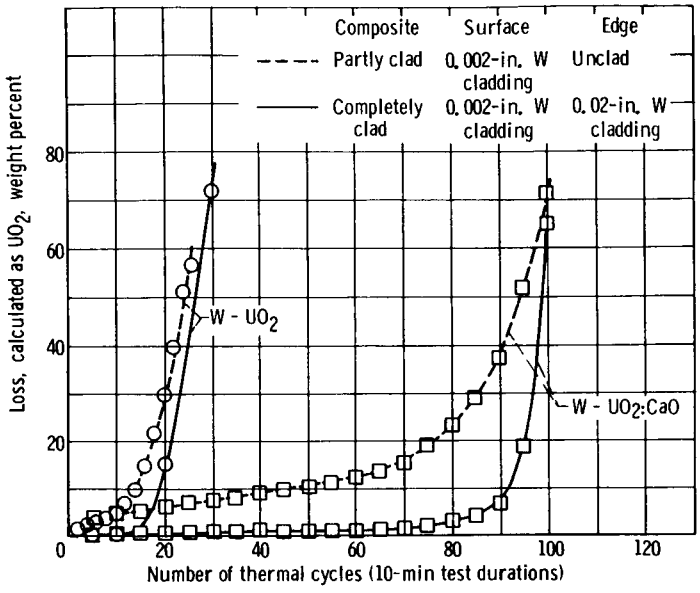

Figure 22. - Effect of cladding on thermal cycling of tungsten - 20-volume-percent uranium dioxide composites subjected to heat treatments at 2500° C in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Fuel particle size, about 50 microns.

migration and vaporization of the decomposition and reaction products.

A series of completely clad composites was thermally cycled to eliminate the effects of edge losses. A comparison of the thermal-cyclic behavior of partly clad and completely clad W - 20-volume-percent UO_2 composites is shown in the fuel loss data of figure 22. As is apparent in these data, complete cladding of composites eliminated the initial vaporization fuel losses observed with partly clad composites, reduced the rate of fuel loss, and substantially increased the cyclic life of the composites, especially for the W-UO_2:CaO composites. The improved performance of the completely clad composites is believed to be a result of maximizing the transport time required for migration and vaporization of the decomposition and reaction products.

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