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TUNGSTEN URANIUM DIOXIDE (W-UO₂)
COMPOSITES BY DEPOSITION FROM TUNGSTEN
HEXAFLUORIDE (WF₆), TASK 1 Summary
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TUNGSTEN CLADDING OF TUNGSTEN-URANIUM DIOXIDE (W-UO₂) COMPOSITES BY DEPOSITION FROM TUNGSTEN HEXAFLUORIDE (WF₆)

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Task 1 Summary Report

by

J.T. Lamartine and A.W. Hoppe

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
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TUNGSTEN CLADDING OF
TUNGSTEN-URANIUM DIOXIDE (W- UO_2) COMPOSITES BY
DEPOSITION FROM TUNGSTEN HEXAFLUORIDE (WF_6)
(~~Top~~ Unclassified)

by
J. T. Lamartine
and
A. W. Hoppe

TASK I SUMMARY REPORT

Covering the Period

June 26, 1964 to February 15, 1965

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TUNGSTEN CLADDING OF
TUNGSTEN-URANIUM DIOXIDE (W- UO_2) COMPOSITES BY
DEPOSITION FROM TUNGSTEN HEXAFLUORIDE (WF_6)
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TASK I SUMMARY REPORT
NASA Contract NAS 3-5218

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Very truly yours,

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Structural Materials and Processes

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ABSTRACT

A program is being conducted to develop a process for cladding tungsten and tungsten cermet fuels with tungsten deposited from the vapor state by the hydrogen reduction of tungsten hexafluoride. Early work was performed using recrystallized, high purity, commercial tungsten as the substrate material. Temperatures in the range 660 to 1295°F (350 to 1700°C) and pressures from 10 to 350 mm Hg were investigated. Hydrogen to WF_6 ratios of 10:1 to 150:1 were utilized. Efforts were directed toward optimizing deposition process parameters to attain control of qualities such as coating thickness, uniformity, density, impurity content, and surface quality. Substrate penetration methods have been investigated in the interest of completely eliminating the interface between the fueled substrate and cladding. In addition, the effects of process parameters and post-cladding heat treatments on the fuel retention properties of clad composites at 4500°F (2480°C) in hydrogen for 2 hours have been evaluated.

As a result of work performed during the first phase of the program it has been shown that the rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be varied in a predictable and reproducible manner by exercising control over the temperature, pressure, and gas flow rates at which the deposits are produced. A significant result of the study is the discovery that substrate nucleation and epitaxial growth in deposits made on both unfueled tungsten and fueled substrates may be effected by pretreating the substrates in hydrogen. High temperature fuel retention testing of tungsten clad W- UO_2 at 4500°F (2480°C) in hydrogen for 2 hours has demonstrated that the vapor deposited layer effectively and consistently restricts fuel loss.

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SUMMARY

The NASA-Lewis Research Center is studying the feasibility of a water moderated nuclear reactor for space propulsion. This reactor, which will use a tungsten-uranium dioxide (W- UO_2) dispersion fuel and hydrogen gas propellant, is expected to operate at temperatures up to 5000°F (2760°C) for times of at least 2 hours. To preclude gross fuel losses at operating temperature due to the high vapor pressure of UO_2 , the intricate fueled bodies will be clad with a thin layer of tungsten. To this end, a program is being conducted at the Westinghouse Astronuclear Laboratory to develop a process for cladding W-20v/o UO_2 composites with vapor deposited tungsten by reducing tungsten hexafluoride gas (WF_6) with hydrogen. Efforts at WANL have been directed toward optimizing deposition process parameters to attain control of qualities such as coating thickness, uniformity, density, impurity content, and surface quality. Substrate preparation methods have been investigated in the interest of completely eliminating the interface between the fueled substrate and cladding. In addition, the effects of process parameters and post-cladding heat treatments on the fuel retention properties of clad composites at 4500°F (2480°C) in hydrogen for 2 hours have been evaluated.

As a result of work performed during the first phase of the program, it has been shown that the rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be varied in a predictable and reproducible manner by exercising control over the temperature, pressure, and gas flow rates at which the deposits are produced. Although both deposition rate and deposit uniformity are influenced by deposition chamber geometry, it has been demonstrated that deposits of over 98% density and of nearly identical quality may be produced on substrates heated either by radiation in a hot wall chamber or by RF induction in a cold wall system with only minimal experimentation being required to transfer technology from one system to the other.

A significant result of the study is the discovery that substrate nucleation and epitaxial growth in deposits made on both unfueled tungsten and W- UO_2 substrates may be effected by pre-treating the substrates in hydrogen at 1600°F (870°C) and 15 mm Hg abs. pressure in the deposition chamber prior to coating. Substrate nucleated deposits of this type have been observed to survive bend testing around a 0.025" radius at room temperature, 800°F (430°C), and 1000°F (540°C) without separation at the substrate-clad interface. Additional work in the area of bonding and deposit structure has revealed that the structure of deposits on W- UO_2 may be altered by recrystallization and that bonding may be improved, as a result of grain growth across the interface, by post-deposition heat treatment at 3600°F (1980°C) for 15 minutes in a vacuum of 10^{-6} mm Hg.

High temperature fuel retention testing of tungsten clad W- UO_2 at 4500°F (2480°C) in hydrogen for 2 hours has demonstrated that the vapor deposited layer effectively and consistently restricts fuel losses to less than 0.15 mg/cm^2 (0.21% of contained UO_2). Microporosity, which is observed in the cladding after exposure to this test and is thought to be caused by low levels of fluorine in the clad, is less apparent in deposits produced at higher temperatures, about

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1295°F (700°C), and in deposits that received post-deposition heat treatment at 3600°F (1980°C) for 15 minutes at 10^{-6} mm Hg. Removal of UO_2 particles exposed to the surface of the W- UO_2 composites by dissolution in HNO_3 prior to cladding to preclude a reaction between the fuel and HF (the product of WF_6 reduction) appears to offer no advantage to improving fuel retention performance in the retention test environment.

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INTRODUCTION

The NASA-Lewis Research Center is studying the feasibility of a water-moderated nuclear reactor for space propulsion. The reactor, which will use a tungsten-uranium dioxide (W-UO₂) dispersion fuel and hydrogen gas propellant, is expected to operate at temperatures up to 5000°F (2760°C) for times of at least 2 hours. To preclude gross fuel losses at operating temperature due to the high vapor pressure of UO₂, the intricate fueled bodies may be clad with a thin layer of tungsten.

To minimize the heat transfer path between fuel and coolant and to reduce the amount of inert structural material in the reactor core, thin cladding is desirable. Cladding thickness of 0.001" to 0.005" could be applied to plates or cylinders as mechanically added sheet or tubular material which could be gas-pressure bonded (or roll bonded in the case of flat plates) to the cermet core. Thin cladding materials in the range of 0.0005" to 0.002", however, would be difficult to apply by this method on more complex shapes. Since presently known cladding methods are applicable to only rather simple shapes, it is mandatory that suitable methods be developed for coating thin, more complex configurations. It is desirable that this cladding satisfy the following minimum requirements.

1. The clad must exhibit a pore-free metallurgical bond to the substrate without the prior interface being discernible.
2. The cladding must be useful up to 5000°F (2760°C) without spalling, cracking, or blistering, and must withstand at least 10 cycles to 4500°F (2480°C), with a total time at temperatures of at least two hours.
3. The coating thickness variation must be within a one-half mil tolerance for thin claddings (less than 0.001") and a one mil tolerance for thicker layers (greater than 0.001").
4. The coating shall be of high purity with no single impurity greater than 50 ppm, and no more than 10 ppm each of the following elements: C, O, S, Be, B, Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn, and Pb. Total halide content shall not exceed 15 ppm.
5. The coating shall inhibit volatilization of the UO₂.
6. The coating shall completely encapsulate the W-UO₂ composite and shall have a minimum density of 18.7 g/cc.
7. The UO₂ loss after two hours in flowing hydrogen at 4500°F (2480°C) shall not exceed 1 mg/cm² of surface area.

To this end, a program is being conducted at WANL to develop a process for cladding W-20 v/o UO₂ composites with vapor deposited tungsten by reducing tungsten hexafluoride gas (WF₆) with hydrogen.

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It is known that tungsten may be deposited from the vapor state from any of several different tungsten compounds⁽¹⁾. Tungsten carbonyl, for example, has been used to successfully yield high quality deposits. Coatings deposited from the carbonyl, however, have been reported to have a higher impurity content, particularly with respect to carbon, than is considered desirable⁽²⁾. Tungsten hexachloride has also been used but requires special equipment for volatilization of the solid chloride prior to injection into the vapor deposition chamber. Impurity levels in tungsten deposited by the reduction of the tungsten hexafluoride have been reported to be substantially less than in deposits made from either the carbonyl or chloride⁽²⁾. The WF_6 compound is easily vaporized at room temperature and can be secured with a relatively high degree of purity. The temperature range for the deposit is not as high nor as critical in its control as the temperature range for deposition from other compounds. These qualities result in a high-density, high-purity deposit^(3,4,5,6,7) that should be quite suitable for cladding W- UO_2 fuels.

Although much work has been done with the hexafluoride process, most of it has been oriented toward the production of tungsten particles and free standing tungsten shapes on expendable mandrels. No standard or best processing procedures presently exist since the process has been employed for widely varying uses and each experimenter has chosen parameters that meet his needs and equipment capabilities. Although some preliminary work had been done on tungsten coated W- UO_2 ⁽¹⁾, direct application of most of the existing technology to cladding fueled compacts was thought not to be possible. Many questions unique to this application remained to be answered. For example, the adherence of tungsten deposits to fueled compacts had never been adequately demonstrated. Another area of question was whether a reaction between HF, the by-product of WF_6 reduction by hydrogen, and the UO_2 would occur during the early stages of deposition⁽⁸⁾ and whether this reaction, if it occurred, would influence the performance of the clad fueled compact in the high temperature, hydrogen reactor environment. Little was reported about specific effects of substrate surface preparation, deposition temperature, reactant flow rates, and reaction pressures on such deposit properties as grain size, deposition rate, deposit density, deposit purity, and adherence.

The program being conducted at Westinghouse has been divided into two phases; the first, demonstration of the feasibility of cladding by this method and the optimization of the coating process; the second, the cladding of fueled samples for environmental testing. Efforts, under Task I, were directed toward optimizing deposition process parameters to attain control of qualities such as coating thickness, uniformity, density, impurity content, and surface quality. Substrate preparation methods have been investigated in the interest of completely eliminating the interface between the fueled substrate and cladding. In addition, the effects of process parameters and post-cladding heat treatments on the fuel retention properties of clad composites at 4500°F (2480°C) in hydrogen for 2 hours were evaluated. The results of Task I are summarized in this report.

DESCRIPTION OF EQUIPMENT AND MATERIALS

Deposition System

A schematic of the vapor deposition apparatus used at Westinghouse is presented in Figure 1. Perusal of the schematic reveals that an induction heated deposition chamber and a resistance heated deposition chamber are connected in parallel with appropriate valving in such a manner that either chamber may be valved out of the system while the other is in use. With this arrangement, metered flows of hydrogen and WF_6 may be simultaneously injected into either chamber where they react to deposit tungsten on a heated sample. After passing through the deposition chamber, the gases flow through a stripping chamber maintained at $1835^\circ F$ ($1000^\circ C$) where the $H_2 + WF_6$ reaction is completed thus removing the balance of the tungsten from the WF_6 vapor. The vacuum pump shown in the system is used to maintain the system at the desired operating pressure. The cold trap between the pump and stripping chamber is maintained at $-115^\circ F$ ($-80^\circ C$) with dry ice and alcohol to preclude back streaming oil vapors entering the deposition chamber and contaminating the tungsten deposit. The gases are exhausted from the pump through a counter-current, water scrubbing column filled with alumina balls where HF , the reaction product, is removed from the stream. Finally, the exhaust hydrogen is burned.

The pressure in the system is monitored with the mercury manometer shown in the schematic. The special arrangements of metering valves, flow meters, and pressure gauges shown in each flow train permit metering the gases at the conditions for which the flow meters were calibrated, viz, $75^\circ F$ and 1 atmosphere.

Special precautions have been taken with the design of this system to maintain lowest possible levels of contamination in the gas stream. Air is excluded from the stream by maintaining the system vacuum leak tight to helium. Hydrogen gas purity is maintained by passing the stream through a palladium catalyst, a drying column, and a liquid nitrogen cold trap before injecting it into the deposition chamber. Although commercial WF_6 is relatively pure, it still contains some undesirable impurities that may be transmitted to the tungsten deposit. All WF_6 cylinders, therefore, are purified by immersing in a dry ice and acetone bath to freeze the WF_6 and evacuating to less than 200 microns to remove volatile impurities. Other steps taken to assure deposit purity are extensive use of copper and stainless steel for piping and chambers and the use of an inert thermoplastic hydrofluorocarbon flowmeter in the WF_6 gas metering train instead of a conventional borosilicate glass flowmeter that is attacked by and contaminates the WF_6 . All other components are standard, commercially available items.

FIGURE 1: Schematic of Tungsten Deposition Apparatus

Support Systems

As shown in Figure 2, three distinct sample support systems have been employed in the coating work done in the resistance heated deposition chamber.

The first system, Figure 2A, consisted of a copper frame with two horizontal copper wires on which to support the 3/4" wide by 3" long unfueled tungsten sample. Deposits made on substrates supported in this manner were consistently of greater thickness on the upper surface than on the downward surface. In addition, the two support wires, although only about 20 mils thick, caused sufficient disruption of the gas flow to shadow the downstream portions of the sample with the result that gross nonuniformities in deposit thickness occurred.

In system two, Figure 2B, the sample was held vertically by three wires in the same copper frame. Deposits produced using this system exhibited good uniformity side-to-side and end-to-end but were prone to shadowing effects on the lower corner of the downstream end due to disruption of the flow in this area by the support frame.

Presently being used, is the system shown in Figure 2C. The samples are supported vertically by 10 mil tungsten wire strung through a half section of 1-1/8" diameter copper tube. Deposits made on samples supported in this manner exhibit over-all uniformity on the order of $\pm 1/2$ mil and shadowing does not occur. One problem still remaining and one which will always remain with any system using static supports for depositing thin films, is that very small uncoated areas are left where the tungsten support wires contact the substrate. With thicker deposits these wires, which would be firmly bonded to the substrate, may be left intact and ground flush with the surface to maintain the continuity of the cladding.

The support system used in the induction heated deposition system is illustrated in Figure 3. This support was comprised of a double teflon spider that formed a tight fit in the vycor tube, an Al_2O_3 rod, and a tungsten wire hook. A small hole was drilled through one end of the sample with micro abrasive blast equipment. The sample was then supported vertically in the chamber from the tungsten hook. During deposition, the sample remained stable and the uniformity of the deposit was not influenced by the support members. Furthermore, since the support components were not heated, either radiantly or inductively, reduction of WF_6 occurred only on the heated sample.

High Temperature Fuel Retention Test System

A schematic of the apparatus used for evaluating the fuel retention properties of tungsten clad W- UO_2 at 4500°F (2480°C) in flowing hydrogen is depicted in Figure 4. As shown in the drawing, this apparatus is essentially a water cooled copper current concentrator enclosed in a vycor pipe and end plate housing. Hydrogen or helium is admitted to the system through the top plate and exhausted through the bottom plate to a two stage oil filled trap designed to remove

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FIGURE 2 Sample Support Systems,
Resistance Heated Systems

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FIGURE 3

Support System Used in Induction Heated Deposition Chamber

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FIGURE 4
Schematic of High Temperature Fuel Retention Test Apparatus

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entrained uranium. The sample under test rests in a tungsten susceptor cup which is covered, top and bottom, with tungsten washers to promote temperature uniformity.

The system is powered by a 50 KW, 350-400 kc RF generator. The temperature of the sample is measured through the sight port in the top plate with a standard optical pyrometer. It was established that black body conditions prevailed within the susceptor cup by experimentation with a black body hole. Corrections for transmission losses through the viewing window and prism were made.

Materials

Hydrogen - Standard, commercially available bottled hydrogen was used for all phases of the work. As described above, hydrogen used in deposition work was passed sequentially through a palladium catalytic deoxygenizing cell, a drying column and a liquid nitrogen cooled cold trap. Hydrogen for the fuel retention test apparatus was taken directly from the producers cylinder without additional purification.

Helium - Helium was used exclusively in the sample cool down phases at high temperature fuel retention testing. As such, it was taken directly from the cylinder.

Argon - Standard commercial argon was used, as delivered from the suppliers cylinder, for those phases of the deposition program requiring a carrier gas. It was also used to purge the evacuated deposition system prior to starting hydrogen flow and furnace heating.

Tungsten Hexafluoride - This material was purchased in 20 pound cylinders. As described above, each cylinder of WF_6 was purified by freezing in a mixture of dry ice and alcohol and then evacuating to less than 200 microns of mercury to remove volatile impurities. An analysis of the WF_6 in two typical cylinders after purification is presented in Table I.

Tungsten Sheet - Tungsten strip, 3/4" wide x 0.032" thick, rolled from powder metallurgy stock was purchased in the hot rolled and pickled condition. To simulate the structure of fueled material as closely as possible, the strip was cut into 3" lengths and recrystallized at 3600°F (1980°C) for 10-20 minutes at 10^{-6} mm Hg.

Tungsten- UO_2 Samples - Thirty-two 3/4" x 3" x .020" sheets of W-20v/o UO_2 were supplied by NASA-Lewis in two batches; twelve sheets in one, twenty sheets in the other. Visual and other examinations revealed slight differences between plates from the two batches. The surface of the 20 plates in batch 1 was observed to be somewhat rough and light brown in color with occasional areas of even darker color. All of the twelve plates in batch 2 were smooth and metallic bright. The unit cell dimension of UO_2 in plates from batch 1 has been measured by x-ray diffraction (procedure described in Appendix I) to be on the order of 5.426Å

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TABLE I
ANALYSIS OF TUNGSTEN HEXAFLUORIDE

Impurity	Concentration (ppm)	
	Cylinder No. 1	Cylinder No. 2
Ca	9	4
Fe	11	1.7
Mg	0.8	0.5
Ni	0.9	1.0
Si	6.2	5.0
Al	< 1	< 1
B	< 0.5	< 0.5
Cd	< 15	< 15
Co	< 1.5	< 1.5
Au	1.0	< 0.5
Mo	< 1.5	< 1.5

at surface exposed UO_2 and 5.47 Å (theoretical value is 5.468 Å) at UO_2 within the interior of the compacts.

The constricted lattice of UO_2 at the plate surface is indicative of either excess oxygen or the presence of other impurities within the UO_2 . Attempts to reduce excess oxygen from the surface UO_2 by treating the composites in dry hydrogen at temperatures to 2820°F (1550°C) for as long as 24 hours resulted in little or no change in lattice parameters. X-ray fluorescence studies revealed that trace quantities of zirconium were present in the surface layers of the composites but were not present in the interior. It was, therefore, concluded that zirconium, introduced in the fabrication process as ZrO_2 sintering barriers, was responsible for the observed UO_2 lattice constrictions. Similar x-ray work with the batch 2 compacts revealed a lesser degree of lattice constrictions and reduced zirconium peaks on the surface layers.

EXPERIMENTAL PROCEDURES

Efforts under Task I of the contract were directed toward optimizing parameters of the coating process to attain control over such qualities as deposit thickness, uniformity, density, imperviousness, impurity content, rate of build-up, and surface quality. In the interest of completely eliminating the interface between the cermet substrate and the tungsten cladding, substrate preparation methods and post deposition heat treatments were evaluated. To obtain a uniform integral coating on all surfaces of the substrate, several methods of supporting specimens were evaluated. Finally, the fuel retention properties of continuous tungsten coatings deposited on W-20% UO_2 compacts were evaluated by testing in hydrogen at 4500°F (2480°C) for two hours.

To attain these ends, initial deposits were made on recrystallized, unfueled tungsten substrates in the resistance heated system described above. Temperatures and pressures in the range 660°F to 1295°F (350°C to 700°C) and 10 to 360 mm Hg were investigated. Hydrogen to WF_6 ratios of 10:1 to 150:1 were utilized. Optimum parameters within the above ranges were developed for cladding unfueled tungsten by systematically varying each parameter followed by an evaluation of the resultant deposit. For this portion of the program, deposit evaluation typically consisted of micrometric measurements for thickness and uniformity and metallographic examination to define the deposit microstructure.

Concomitant with these studies, the effects of substrate preparation on the nature of the bond between substrate and cladding were considered. Predeposition substrate preparations that were evaluated consisted of the following:

1. Degreasing with acetone.
2. Etching in a solution of 60% HF-40% HNO_3 to remove 0.001" per side.

3. Oxide reduction treatment in the deposition chamber at 1600°F (870°C) in hydrogen for 15 minutes at about 15 mm Hg absolute pressure.
4. Etching in 60%HF-40%HNO₃ per (2) followed by the hydrogen reduction treatment described in (3).

Deposits which were made on substrates pretreated per the above methods were evaluated metallographically to define the nature of the bond. The relative adherence of the deposit to the substrate was demonstrated by the ability of the deposit to survive abrasive disc sectioning or bending around a 0.025" radius at temperatures from room temperature to 1000°F (540°C).

In addition to establishing the relationship between substrate preparation and bonding, the effects of post deposition thermal treatment on enhancement of the clad-substrate bond were studied. Unfueled tungsten samples clad under a wide range of parameters, following pretreatment per the four methods outlined above, were given a 15 minute thermal treatment at 3600°F (1980°C) at 10⁻⁶ mm Hg and subsequently evaluated metallographically to detect improvements in the nature of the interface or deposit structure.

At this juncture, the applicability of the parameters and processes developed with plain tungsten to cladding the NASA supplied W-20V/oUO₂ composites was demonstrated. In addition, studies were performed in which both fueled and unfueled samples were clad in the RF induction heated system to define the applicability of procedures and parameters developed with the resistance heated system.

The fuel retention test program, which was conducted in the apparatus shown in Figure 4, was designed to evaluate the effects of deposition parameters, precladding surface treatments, and post cladding thermal treatments on the fuel retention properties of clad, NASA supplied, W-20V/oUO₂ composites. All of the samples tested were clad in the resistance heated system. Fuel retention testing was performed for 2 hours at 4500°F (2480°C) in flowing hydrogen according to the following plan:

1. Load the weighed and measured samples into the system, purge with helium for 5 minutes minimum then purge with hydrogen for 5 minutes minimum.
2. Heat to 3000°F (1650°C), 2 minutes to temperatures and hold for 30 minutes. Cool to room temperature in helium.
3. Weigh and measure samples.
4. Load samples into system. Purge with He and H₂ per step (1).
5. Heat to 4500°F; time to temperature 1 minute. Hold 2 hours.
6. Cool to 2000°F (1095°C) in H₂. Purge system with He.
7. Cool from 2000°F (1095°C) to room temperature in He.

Tested samples were weighed and measured to define weight and dimensional changes, sectioned, and examined metallographically to evaluate changes in microstructure. In addition, several samples were bend tested at 1000°F (540°C) to evaluate post test cladding adherency.

RESULTS

The results of experimental work performed during the first phase of the contract are discussed in the following sections.

Deposition Rate

The basic parameters that define and control the pyrolytic deposition of tungsten from WF_6 are temperature, pressure, WF_6 flow rate, and hydrogen flow rate. Of these four parameters, it has been found that temperature and pressure exhibit the greatest influence on the rate at which tungsten is deposited on the substrate.

The rate of tungsten deposition as a function of system pressure is illustrated in Figure 5. As shown in this graph, the rate of build-up of pyrolytic tungsten at 915°F (490°C) appears to exhibit a logarithmic dependency on the pressure at which the deposit is made. From the structural standpoint, thin deposits made at low pressures exhibit the same microstructure as deposits made at high pressure. No voids or microporosity were observed at magnifications up to about 500X in any of the deposits regardless of deposition pressure within the range studied.

The effects of pressure on deposition rate are further illustrated in Figure 6 which shows the interrelationship between temperature and deposition rate as determined in the resistance heated system at average system pressures of 20 mm and 40 mm of Hg. At both pressures, the deposition rate increases linearly with temperature over the range of temperatures investigated. Comparison of the two curves reveals that at the lower pressure the effect of temperature on the rate of deposition is reduced. This observation has at least two important implications. First, extrapolation of the two curves to zero deposition rate indicates that the minimum temperature at which deposition will occur may be lowered by operating the system at lower pressure. Secondly, low system pressure allows greater control over deposit thickness at higher deposition temperatures.

Metallographic examination has shown that thin deposits produced in this study appear to be identical in nature regardless of deposition rate. All deposits appeared to be dense with no entrapped voids or microporosity. Experience with one sample coated at 1185°F (640°C) and 40 mm Hg has indicated that, at rates greater than 16 mils/hour, growth becomes markedly dendritic and results in the entrapment of voids between the dendrites. This sample was not included in the data presented in Figure 6 because the system used to support the substrate influenced the thickness of the deposit. One difference between deposits made at high and

low deposition rates has been observed. In the interest of clarity of presentation, this observation will be discussed in the section concerning surface preparation and crystal growth.

It has been observed that the rate of tungsten deposition in the RF induction heated system falls within the range predicted by the data presented in Figures 5 and 6. Rate versus temperature is illustrated in Figure 7. As shown in the graph, deposition rate in the induction heated system varied as a linear function of temperature. As predicted from the pressure relationship graph shown in Figure 6, the experimental curve for induction heating at 27 mm Hg system pressure falls on the theoretical point.

Reproducibility

It has been determined that at any given set of operating parameters (pressure, temperature, and measured flow rates) tungsten deposits of predetermined thickness may be consistently produced provided allowances are made for increases in the linear flow rate induced by changes in the cross section of the heated deposition chamber as subsequent depositions reduce its diameter. Experience gained from over 90 deposition runs indicates that as the diameter of the resistance heated deposition chamber decreases, the rate at which tungsten is deposited increases. No specific measure of this effect has been made; however, it can be illustrated by review of the data presented in Table II. From the data of runs 62 through 65, it can be seen that the deposition rate was relatively constant at about 1.5 mils per hour at a deposition temperature of 896°F (480°C). In runs 66 through 68, rather heavy deposits were made at a higher temperature causing a reduction in the chamber diameter as tungsten was deposited on the hot walls. As the chamber diameter became constricted during these three runs, the deposition rate, at 535°C, increased from 2.5 to 6.0 mils/hour. Following these heavy deposits, deposition was again continued at 896°F (480°C); however, chamber constriction had caused the rate to increase to about 2.3 mils/hour. It is difficult to make qualitative measures of the change in deposition rate with deposition chamber constriction because of other, non-measurable, attendant effects such as warping of the muffle and copper boat as the deposited layers increased.

This shift in deposition rate, on the other hand, does not present a significant problem to one's ability to reproducibly deposit tungsten layers of desired thickness. Once the basic rates have been established for a set of operating parameters, thickness control may be maintained by basing the deposition rate for any run on the rate calculated from the preceding run. The degree to which deposit thicknesses may be controlled in this way is demonstrated by the data presented in Table III.

This problem does not exist with the induction heated system since tungsten is not deposited on the cold chamber walls.

FIGURE 5

Pyrolytic Tungsten Rate as a Function of Pressure at Constant
Temperature and Flow Rate for Resistance Heated System

FIGURE 6

Pyrolytic Tungsten Deposition Rate as a Function of Deposition
Temperature and Pressure for Resistance Heated System

FIGURE 7

Pyrolytic Tungsten Deposition Rate as a Function of Deposition Temperature and Pressure for Induction Heated System

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TABLE II
VARIATION OF DEPOSITION RATE WITH BUILD-UP
OF DEPOSITS ON DEPOSITION CHAMBER WALLS

Run No.	Deposit Thickness (mils)	Deposition Temp. °C	Deposition Time (min.)	Average Deposition Rate (mils/hr)	Deposition Chamber Diameter Change (mils from Run 62)
62	0.5	480	20	1.5	0
63	0.9	480	35	1.58	-1
64	1.7	480	65	1.57	-2.8
65	1.55	480	65	1.42	-6.2
66	17.5	535	420	2.5	-9.3
67	32	535	425	4.5	-44.3
68	18	535	180	6.0	-108.0
69	3.4	480	60	3.4	-144.0
70	1.2	480	35	2.1	-146.5
71	1.6	480	40	2.3	-149.5
72	1.6	480	40	2.3	-152.5

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Uniformity

Two factors have been found to greatly affect the uniformity of pyrolytic tungsten deposits; flow distribution as influenced by the sample support system, and the rate of deposition relative to the linear rate of WF_6 flow past the sample. Minimum flow disruption occurs using the support system shown in Figure 2C thus uniform deposits may be readily produced provided that other processing parameters permit uniform deposition to occur. This leads to the second factor that influences uniformity, WF_6 linear flow rate versus deposition rate. At the higher deposition rates, whether due to increased temperature or increased pressure, the deposit thickness becomes non-uniform; tapering from heaviest at the upstream end to thin at the downstream end. This effect is thought to be due to depletion of WF_6 from the gas stream faster than it is supplied by the linear flow rate down the length of the specimen. At low deposition rates (low pressure and temperature), the reaction rate between hydrogen and WF_6 is relatively slow; thus, depletion of WF_6 from the gas stream as it flows past the sample is relatively low. Increasing the velocity of the WF_6 flowing past the sample by increasing the measured WF_6 flow rate, reducing the chamber diameter, or by introducing an inert carrier gas makes it possible to produce uniform deposits at high deposition rates.

Experience has indicated that deposits 4 to 5 mils thick may be produced on 3/4" wide x 3" long tungsten substrates with a total variation in thickness of less than 1 mil at deposition rates up to about 4 mils per hour using hydrogen and WF_6 measured flow rates of 1000 cc/min and 100 cc/min respectively. At rates greater than about 4 mils/hour, increased WF_6 flow is required to maintain the same level of uniformity. Typical variations in the thickness of deposits made at rates less than 4 mils/hour are illustrated by the data previously presented in Table III.

It should be noted that one important ramification of achieving uniform deposits over relatively long lengths, without resorting to complex temperature profiles or moving hot zones, is that the process must be operated non-efficiently. The thickness of the deposit made on any increment of length appears to be directly dependent upon the amount of WF_6 available to it. For maximum uniformity, depletion should be minimized; therefore, efficiency will be low.

Surface Preparation and Crystal Growth

Metallographic examination of deposits made under comparable conditions on recrystallized, unfueled tungsten samples pre-treated in different manners revealed marked differences in both the structure of the deposits and in the degree of interface obliteration. Figure 8 presents a photomicrograph of a deposit made on a substrate that was just degreased with acetone prior to coating. This deposit can be characterized as being columnar in structure with a readily discernible interface between coating and substrate. The structure of this deposit is quite like those made on the walls of the stainless steel plating chamber (see Figure 9 for comparison). This crystalline growth pattern is expected when the tungsten cannot assume the orientation of the crystal lattice of the substrate. Deposits of this nature have been prone to fracture of the interface during sectioning with an abrasive wheel for metallographic preparation.

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TABLE III
REPRODUCIBILITY OF PROCESS

<u>Run Number</u>	<u>Range of Actual Deposit Thickness (Mils)</u>	<u>Desired Thickness (Mils)</u>	<u>Range</u>
73	0.55 - 0.80	0.5 - 1	0.15 - 0.30
74	0.45 - 0.60	0.5 - 1	
75	0.75 - 0.90	0.5 - 1	
84	0.85 - 1.15	0.5 - 1	
87	0.75 - 0.95	0.5 - 1	
80	1.0 - 1.4	1 - 2	0.20 - 0.65
81	1.1 - 1.55	1 - 2	
83	1.1 - 1.5	1 - 2	
65	1.3 - 1.55	1 - 2	
89	1.1 - 1.75	1 - 2	
77	4.1 - 5.0	4 - 5	0.15 - 0.90
78	4.6 - 4.75	4 - 5	
88	4.2 - 4.6	4 - 5	
93	4.5 - 5.07	4 - 5	
94	4.1 - 5.0	4 - 5

400X

Murakami's Etchant

FIGURE 8

Photomicrograph of a tungsten deposit made on acetone degreased tungsten substrate. Note columnar structure of deposit and clearly defined interface. Deposit made at 915°F (490°C), 70 cc/min WF_6 , 4500 cc/min H_2 , 38 mm Hg.

250 X

Murakami's Etchant

FIGURE 9

Photomicrograph of a tungsten deposit taken from walls of the stainless steel plating chamber illustrating natural growth habit of pyrolytic tungsten. Bands are the result of a number of deposition runs.

Figure 10 illustrates the type of deposit produced on a substrate that was etched in 60% HF-40% HNO_3 prior to coating. The columnar growth habit and the clearly distinguishable interface indicate that substrate nucleation did not occur. As with the degreased sample, this sample tended to fracture at the interface during sectioning.

A typical deposit made on a sample given the hydrogen reduction treatment(3) prior to deposition is shown in Figure 11. Examination of the structure of the deposit reveals an obvious lack of the columnar structure and a high degree of substrate nucleation and epitaxial growth. For the most part, the interface between the deposit and substrate is nearly obliterated. It is postulated, as a result of extensive examination of samples produced in this manner, that epitaxial growth of the deposit occurs on substrate grains whose orientation closely approximates the natural growth orientation of pyrolytic tungsten. On grains whose orientation widely differs from the deposit, epitaxial growth seems to begin but is apparently superceded by the natural growth habit of the deposit and the columnar structure results. The hydrogen reduction pre-treatment provides the requisite clean, oxide-free surface on which substrate nucleation may occur.

As shown in Figure 12, the same high degree of epitaxial growth was observed in deposits made on substrates prepared by etching in 60% HF-40% HNO_3 followed by the hydrogen reduction pre-treatment.

An additional factor that appears to influence the nature of the bond between the deposit and substrate and the degree of epitaxial growth is the ratio of hydrogen flow to WF_6 flow. Metallographic examination of deposits made on etched and hydrogen pretreated substrates at $\text{H}_2:\text{WF}_6$ ratios from 10:1 to 150:1 suggests that epitaxial growth is most predominant in deposits made at low ratios and slow rates of growth. Comparison of the photomicrographs presented in Figures 13 and 14 illustrates this effect. Figure 13 shows the microstructure of a deposit made at an $\text{H}_2:\text{WF}_6$ ratio of 10:1. A high degree of epitaxial growth and complete elimination of the original interface (approximately 90%) can be readily seen in this photograph. Figure 14, which depicts the structure of a deposit made at 150:1 $\text{H}_2:\text{WF}_6$ ratio, shows extensive epitaxial growth but a more readily discernible interface. Specimens coated at intermediate ratios showed intermediate degrees of interface visibility with the trend to being less discernible at lower ratios.

As previously mentioned, the rate at which the deposit is made influences the structure of the deposit to some extent. In a substrate nucleated deposit made at low deposition rates epitaxial growth dominates for the entire thickness of the deposit and flat surfaced grains are formed. In substrate nucleated deposits made at relatively high deposition rates, however, epitaxial growth seems to degenerate into columnar growth after a few mils producing grains with serrated outer surfaces.

From the standpoint of adherence, it is obvious that coatings with a high degree of substrate nucleation will have a higher bonding strength than coatings with non-epitaxial, columnar growth. This point is well illustrated in Figure 15, two photomicrographs of a sample that received rather abusive treatment during sectioning with an abrasive disc. Since cracking

400X

Murakami's Etchant

FIGURE 10

Photomicrograph of a tungsten deposit made on etched (60% HF-40% HNO₃) tungsten substrate. Note columnar growth. Deposit made at 915°F (490°C) 70 cc/min WF₆, 4500 cc/min H₂, 42 mm Hg.

400X

Murakami's Etchant

FIGURE 11

Photomicrograph of pyrolytic tungsten deposit made on a tungsten substrate that was given pre-coating treatment for 5 min. at 1600°F (870°C) in H₂. Note extensive substrate nucleation and epiaxial growth with obliteration of the interface. Deposit was made at 915°F (490°C), 70 cc/min WF₆, 4500 cc/min H₂, 36.8 mm Hg.

400X

Murakami's Etchant

FIGURE 12

Photomicrograph of a tungsten deposit made on a tungsten substrate that was etched in 60% HF 40% HNO₃ followed by 5 min. in H₂ at 1500°F (815°C) prior to coating. Deposit was made at 915°F (490°C), 70 cc/min WF₆ flow, 4500 cc/min H₂, 66 mm Hg.

50CX

Murakami's Etchant

FIGURE 13

Tungsten deposit made at $H_2:WF_6$ ratio of 10:1 on etched and H_2 pretreated tungsten substrate showing extensive epitaxial growth and complete obliteration of interface. Deposition parameters were $915^\circ F$ ($490^\circ C$), WF_6 -50 cc/min, H_2 -500 cc/min, pressure - 31 mm Hg.

400X

Murakami's Etchant

FIGURE 14

Tungsten deposit made at $H_2:WF_6$ ratio of 150:1 on etched and H_2 pretreated tungsten substrate. Note epitaxial growth and presence of definable interface. Deposition parameters: $915^\circ F$ ($490^\circ C$), 6000 cc/ H_2 , 40 cc/min WF_6 , 46 mm Hg.

400X

Murakami's Etchant

400X

Murakami's Etchant

FIGURE 15

Photomicrographs of a longitudinal section through a sample that received unusually rough treatment during abrasive disc sectioning showing that the coating bond strength may exceed intergranular strength. This deposit was made at 915°F (490°C), WF_6 flow 70 cc/min, H_2 flow - 4500 cc/min, at 42 mm Hg pressure on a hydrogen pretreated substrate.

occurred in the substrate during sectioning, it is apparent that the strength of the bond between cladding and substrate is at least equal to intergranular bonding strength in some areas.

It has been demonstrated that the 1600°F (870°C) hydrogen pretreatment prior to deposition in either radiant heated or induction heated system is as effective for promoting excellent bonding and epitaxial growth on W-20%UO₂ composites as it is for unfueled, recrystallized tungsten. Photomicrographs of typical deposits made on NASA supplied W-UO₂ composites pretreated in hydrogen prior to cladding are presented in Figures 16 and 17. As seen in the photomicrographs, the bond between the core and cladding is excellent and a high degree of interface obliteration is evident. Little difference exists between radiant and induction heated samples. Typically, the structure of deposits made on fueled substrates is about 50% columnar and 50% epitaxial. As predicted by previous experiments, deposits on the composites exhibit a columnar growth habit over UO₂ particles that are exposed at the interface because the crystal structure of the UO₂ is not conducive to substrate nucleation. This effect is illustrated in Figure 18. Figure 18 also provides an example of the throwing power of the process in that it shows that the vapor deposited tungsten penetrates and fills voids and cracks that are exposed to the original compact surface. This is further illustrated by Figure 19, a section through the hole and support wire of a sample coated in the induction heated system. It is readily observed that the deposited tungsten has penetrated into the gap between the hole and wire and completely sealed the support wire into the composite. The implications of this observation to joining and cladding intricate fueled composites are only limited by ones imagination.

Density

Metallographic examination of all deposits made over a wide range of parameters in both systems has indicated that the deposits are free from voids and porosity and approach theoretical density. The density of a 5 to 10 mil thick tungsten deposit produced on a copper mandrel has been determined to be 19.4 g/cm³. This determination was made by the water displacement method after the copper mandrel had been dissolved. Although the measured value of 19.4 g/cm³ is greater than the recognized value of 19.3 g/cm³, it is within the limits of accuracy of the determination and indicates that the density of the deposit closely approached theoretical density. The x-ray density of tungsten deposits has been determined to be 19.245 g/cm³.

Bend Tests

To demonstrate the adherence of vapor deposited tungsten to plain and fueled tungsten substrates, a series of bend tests were run at temperatures from room temperature to 1000°F (540°C). In these tests 2" x 3/4" coated samples were heated to the specified temperatures and then bent around a 0.025" radius over a 0.75" span in a tensile testing machine. Both unfueled, recrystallized tungsten and W-UO₂ samples coated at temperatures from 660°F (350°C) to 1295°F (700°C) were tested. All samples were pretreated at 1600°F (870°C) in hydrogen in the deposition chamber prior to cladding with tungsten.

400X

Murakami's Etchant

FIGURE 16

Photomicrograph of pyrolytic tungsten deposit on W-20 v/o UO_2 produced in radiant heated system. Following pre-treatment in H_2 at 1600°F (870°C) for 15 mins.

40CX

Murakami's Etchant

FIGURE 17

Photomicrograph of pyrolytic tungsten deposit on W-20 v/o
 UO_2 produced in induction heated system following pre-
treatment in H_2 at 1600°F (870°C) for 15 mins.

400X

Murakami's Etchant

FIGURE 18

Photomicrograph of pyrolytic tungsten deposit on W-20 v/o UO_2 . Note columnar growth habit of deposit on UO_2 particle at the interface and penetration of tungsten into voids and cracks in the UO_2 .

100X

As Polished

FIGURE 19

Section through hole and support wire in W-UO₂ sample
coated in the induction heated system.

Metallographic examination of sections through the bend area in each of the samples revealed that in no instance did the coating separate from the substrate during the test. Photomicrographs of typical samples are presented in Figures 20 through 22.

Post Deposition Heat Treatment

It has been observed that the quality of the bond between the deposit and substrate and the microstructure of the deposit may be altered by post-deposition heat treatment. Figure 23 illustrates a tungsten deposit made on a degreased substrate. As such, the deposit is columnar in structure with a readily discernible interface. This same deposit, after recrystallization at 3600°F (1980°C) for ten minutes at 10^{-6} mm Hg pressure, is shown in Figure 24. From the photomicrograph, it can be seen that extensive recrystallization has occurred in the deposit and that grain growth has proceeded across the original interface.

Extensive metallographic examination of several unfueled tungsten samples clad under conditions that were not conducive to substrate nucleation and good bonding indicated that they were prone to fracturing at the clad-substrate interface during sectioning with an abrasive cut-off wheel. After heat treatment for 10 minutes at 3600°F (1980°C) in vacuo, sections from the same samples, which then exhibited enhanced bonding, did not fracture at the interface during sectioning.

Microhardness of Tungsten Deposits

The hardness of tungsten deposits produced under several sets of parameters is presented in Table IV. Comparing the deposit hardness values on the basis of temperature one finds that deposit hardness tends to increase slightly with deposition temperature. Examination of the data for the as-deposited versus the post-deposition, heat treated condition of 3600°F (1980°C) for 10 minutes in vacuum reveals that the hardness of the tungsten deposit is reduced by this thermal treatment.

Non-Destructive Testing

A limited non-destructive testing study was conducted to determine whether or not the quality of the bond between clad and substrate could be readily defined. Coated, unfueled, tungsten substrates embodying degrees of clad bonding from non-adherent mechanical bonding produced on an oxidized substrate to tightly adherent epitaxially grown deposits were examined in this study. These samples were evaluated by eddy current techniques and by pulse echo ultrasonic techniques at 5, 19, 15, and 25 mc using a 3/8" diameter crystal with the result that no definable difference was detected between samples over the complete range of bonding. Lack of ability to define varying degrees of bonding using these techniques has also been observed by workers at Battelle-Northwest⁽⁹⁾.

100X

As Polished

FIGURE 2C

Tungsten clad $W-UO_2$ composite after bend testing at room temperature.

75X

Murakami's Etchant

FIGURE 21

Tungsten clad plain tungsten after bend testing at
800°F (430°C).

10CX

Murakami's Etchant

FIGURE 22

Tungsten clad $W-UO_2$ after bend testing at $1000^{\circ}F$ ($550^{\circ}C$).

400X

Murakami's Etchant

FIGURE 23

Section of deposit made on an unfueled, recrystallized tungsten substrate that was just degreased prior to plating.

400X

Murakami's Etchant

FIGURE 24

Section through same sample shown in Figure 23 after
recrystallization at 3600°F (1980°C) for 10 minutes in vacuo.

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TABLE IV
MICROHARDNESS OF VAPOR DEPOSITED TUNGSTEN

Sample No.	<u>36</u>	<u>35</u>	<u>34</u>	<u>18</u>	<u>24</u>	<u>78</u>	<u>23</u>	<u>Avg.</u>
Depo. Temp. (°C)	360	450	550	490	490	480	490	
Substrate	WK-126	WK-126	WK-126	KD-1169	KD-1169	WK-126	W-UO ₂	
Microhardness (DPH, 50 Kg load)								
Clad (as deposited)	498,488	597	622,564	645,612	543,780		543,597	595
Core (as deposited)	472,487	498,405	492,472	421,401	433,449		429,342	
Clad (post depo. H. T.) ⁽¹⁾				482,487	425	390,524		465
Core (post depo. H. T.) ⁽¹⁾				449,405	342,390	612,449		

⁽¹⁾ 3600°F (1980°C) for 10 min. at 10⁻⁶ mm Hg.

Fluorescent penetrant inspection of 0.0005" to 0.005" thick deposits produced on both unfueled, recrystallized tungsten and on W-20 v/o UO_2 composites has revealed no detectable defects.

Impurity Content

Analytical data on the impurity content of tungsten deposits produced on unfueled, recrystallized tungsten substrates are presented in Table V together with an analysis of the substrate material. Analyses for the elements listed were performed using the entire sample, i.e., both substrate and deposit; therefore, to define the concentration of each element in the deposit alone, the reported data had to be proportioned.

Perusal of the table reveals that with the exception of Cu, Si, C, and possibly Ca and F, the concentration of each of the 26 elements sought is less than 10 ppm. The presence of up to 19.8 ppm copper in the deposits may be the result of copper pick-up from the copper tubing used extensively in the deposition system. The silicon determinations listed are seriously questioned due to the wide discrepancy between the values reported by Westinghouse and the substrate supplier. The source of carbon concentrations of 22 ppm and 32.5 ppm in the deposits is thought to be oil that back streams from the vacuum pump in the system. Although the cold trap in the system is maintained at about -115°F (-80°C) with dry ice and alcohol to preclude back streaming, two possible factors in favor of back streaming oil contamination may be postulated. First, the trap might not be sufficiently efficient to completely eliminate back streaming. Secondly, at this point in the program, the system was evacuated to less than about 25μ prior to filling the cold trap. It is therefore possible that back streaming had already occurred to an extent capable of causing the measured carbon contamination.

It is disconcerting that the limits of detection for the methods used by one analytical laboratory to determine calcium and fluorine levels are 100 ppm and 20 ppm respectively. Review of the system components and source materials, however, indicates that calcium concentrations in the deposit should be rather low since no sources of this element can be conceived. With regard to fluorine, it may just be said, at this juncture, that the concentration of fluorine in pyrolytic tungsten deposits made on unfueled, recrystallized tungsten is less than 20 ppm.

Due to the possibility of a reaction between fluorides in the gas stream and UO_2 exposed to the surface of W- UO_2 compacts during vapor deposition of the cladding, additional work on fluorine contamination was performed in this area at a second analytical laboratory. Fluorine concentrations for two W-20 v/o UO_2 samples, one clad at 985°F (480°C), the other clad at 1295°F (700°C), are presented in Table VI along with fluorine assays for the as-received W- UO_2 compacts. These data may be interpreted in two ways. First, it may be assumed that the fluorine is combined with uranium at the clad core interface in the form of UF_4 . If this is the case, the similar total fluorine concentrations of 2.8 and 3.0 suggest that fluorine pick-up at both temperatures is

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TABLE V
IMPURITY CONTENT OF VAPOR DEPOSITED TUNGSTEN
Concentration (ppm)

Sample	WK-126	WK-126-47	WK-126-51
Deposit to Substrate Wt. Ratio	As-Received	2.5/1	5.5/1
Element			
Al	5	3	3
Mg	120	7	2
Cu	5	11.5	19.8
Fe	34	4	3
Ni	5	4	3
Si	> 150	37	37
Be	< 5	5	< 5
B	< 5	5	< 5
Na	3.95	0.9	6
Ca	< 100	< 100	< 100
Ti	< 5	< 5	< 5
V	< 5	< 5	< 5
Cr	< 5	< 5	< 5
Mn	< 5	< 5	< 5
K	0.81	0.47	2.6
Zr	< 5	< 5	< 5
Mo	< 10	< 10	< 10
Cd	< 5	< 5	< 5
Sn	< 5	< 5	< 5
Pb	< 5	< 5	< 5
N ₂	< 5	1	13
O ₂	9	4.4	4.6
C	81	22	32.5
Co	< 1	< 1	< 1
S	8	8	8
F	< 20	< 20	< 20

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TABLE VI
FLUORINE CONCENTRATION IN W-20% UO_2 COMPACTS
CLAD WITH TUNGSTEN BY VAPOR DEPOSITION FROM WF_6

Sample	Cladding Temp.	Wt. Ratio - Clad to Substrate	F Concentration (ppm)	
			Total Sample	Clad Only as Extrapolated on Basis of Wt. Ratio
53	700°C	1.55/7.87	3.0	15.2
54	480°C	.25/6.73	2.8	75.5
1	Not Clad	--	<1	--
2	Not Clad	--	<1	--

equal since the starting samples were of equal area. On the other hand, if it is assumed that the fluorine is uniformly distributed throughout the deposits, the fluorine concentrations in the 895°F (480°C) deposit, as proportioned on the basis of clad-to-substrate weight ratios, greatly exceeds that found in the 1295°F (700°C) deposit; i.e., 75.5 ppm and 15.2 ppm respectively. Fluorine distributed throughout the cladding is probably in the form of WF_4 or WF_5 rather than UF_4 . Although information exists to support either premise, none of it is sufficient to resolve which case prevails. Clearly, additional work in this area is required to resolve the question.

Fuel Retention Testing

In the interest of providing a concise and complete presentation, it is in order at this point to discuss the reasoning that led to the selection of samples for high temperature fuel retention testing. A summary of the relationship of parameters to desirable cladding qualities is tabulated in Table VII. In reviewing this table, it is readily seen that a high degree of consistency exists amongst the parameters for satisfying the listed requirements. If the factors that favor precluding a reaction between UO_2 and HF are excluded, it is seen that low H_2/WF_6 ratio, low temperature, low pressure, and pretreatment at 1600°F in H_2 will yield deposits that will probably meet the remainder of the requirements. High H_2/WF_6 ratio, high temperature (in excess of 1295°F (700°C)) and removal of the UO_2 from the surface of the compact by acid etching or vacuum extraction are factors which inhibit fluorination of UO_2 particles exposed to the surface of W- UO_2 compacts. It was with this information in mind that the fuel retention test samples were clad with pyrolytic tungsten and subsequently tested at 4500°F (2480°C) in flowing hydrogen for 2 hours.

Results of these tests are presented in Table VIII. Weight losses from the clad compacts resulting from exposure to hydrogen at 4500°F (2480°C) were extremely low; so low that the weight changes noted bordered on the lower limit of sensitivity of the balance. Analysis of these data as a function of deposition parameters reveals that the measured weight losses are all of the same order of magnitude regardless of the conditions at which the cladding was deposited. Furthermore, the predicted beneficial efforts of post deposition heat treatment and removal of surface UO_2 are not reflected in these data.

Metallographic examination of samples after the fuel retention test has proven to be significantly more definitive than weight loss data for revealing subtle differences in the behavior of deposits produced at various parameters. Figure 25 is a photomicrograph of a longitudinal section of W-20% UO_2 with as deposited tungsten cladding applied at 895°F (480°C), 10:1 H_2/WF_6 ratio. Figure 26 is a similar sample, No. 56 with clad deposited at the same conditions, after testing for 2 hours at 4500°F (2480°C) in flowing hydrogen. Of specific interest in this photo is the porosity present in the clad after the test. Attention is also called to the apparent densification of the UO_2 during the test and the extensive grain growth within the tungsten matrix of the composite. These three effects were common to all of the clad composites tested. Fuel densification and grain growth with the W- UO_2 compacts

TABLE VII
Factors Favoring Meeting Cladding Requirements

Requirement	Deposition Parameters Favoring Meeting Requirements				
	H_2/WF_6 Ratio	Temperature (°C)	Pressure (mm Hg)	Pretreatment	Other
Good Bonding	Low	Low	Low (< 20 mm)	15 mins. in H_2 at 1600°F	Favored by slow growth rate
High Density	Probably optional	Low	Low	Optional	Favored by slow growth rate
Uniformity	(Ratio of WF_6 flow rate to deposition rate - parameters can be arranged.)				
Grain growth-optional	Low	Low	Low	15 mins. in H_2 at 1600°F	Favored by slow growth rate
-columnar	Optional	Optional	Optional	Degrease only	Not consistent with good bonding
No fluorination of UO_2	High	> 700	Low	Optional	Removal of surface UO_2 by acids or vacuum extraction.
Impurity Level	Probably optional	Optional	Low	Optional	Gas purity, system cleanliness, system leak tightness.
Freedom from cracks	(Consistant with good bonding and relative coefficients of thermal expansion of substrate and cladding.)				

- (1) It might be possible to produce adherent columnar deposits by beginning deposition using parameters that favor good bonding then change to parameters favoring rapid growth.

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TABLE VIII
Results of Fuel Retention Testing of W-UO₂ Clad with Vapor Deposited Tungsten

Sample No.	Ratio	Temp. (°C)	Parameters (1) Pressure (mm Hg)	Post Deposition Heat Treatment (2)		Wt. Loss after 2 Hrs. at 4500°F in H ₂		Remarks
				Yes	No	mg/cm ²	% of Contained UO ₂	
56	10/1	480	17		X	.069	.106	
56-1	10/1	480	17	X		.077	.115	
71	10/1	480	17		X	.131	.210	UO ₂ removed from surface with HNO ₃
72	10/1	480	17	X		.119	.186	UO ₂ removed from surface with HNO ₃
57	8/1	700	17		X	.082	.127	700° deposit less than 1 mil thick
	10/1	480	17					
55	8/1	700	17		X	.057	.098	700° deposit less than 1 mil thick
	10/1	480	17					
57-1	8/1	700	17	X		.074	.120	700° deposit less than 1 mil thick
	10/1	480	17					
59	10/1	480	17		X	.086	.148	.003 abraded from one side prior to cladding to remove Zr contaminated layer.

(1) All samples were pretreated at 1600°F (870°C) in H₂ for 15 mins. prior to cladding.

(2) 3600°F (1980°C) at 10⁻⁶ mm Hg for 15 mins.

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FIGURE 25

Vapor deposited tungsten on W-20v/o UO_2 compact. As deposited.
Deposition parameters: 895°F (480°C), H_2/WF_6 - 10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2 .

remained relatively constant from sample to sample. Porosity formation in the cladding, as will be subsequently shown, exhibited a consistent dependency on deposition parameters, post deposition thermal treatment, and W- UO_2 composite batch.

Comparison of the photomicrographs in Figure 27 (Sample 56-1) with those shown in Figure 26 illustrates the effect of post deposition heat treatment on the formation of porosity in the cladding. These samples were cut from the same sheet of W- UO_2 stock and clad in the same deposition run. Sample No. 56-1 (Figure 27) was heat treated at 3600°F (1980°C) for 15 minutes in vacuo prior to fuel retention testing. Sample No. 56 (Figure 26) was tested as clad. It is quite obvious that porosity formation is substantially reduced by the post-deposition heat treatment.

The cladding on the sample shown in Figure 28 was deposited at two temperatures. In the interest of precluding a reaction between surface exposed UO_2 in the W- UO_2 compact and the coating gases, a thin layer of tungsten (less than 1 mil thick) was first deposited at 1295°F (700°C). The sample was then cooled to 895°F (480°C) and the remainder of the cladding (about 2 mils) deposited at this temperature at a more readily controlled rate. Porosity formation in the cladding of this sample after exposure to hydrogen at 4500°F (2480°C) is again apparent. It is interesting to note, however, that the porosity is restricted to the thicker tungsten layer deposited at 895°F (480°C). Little porosity exists in the initial thin layer deposited at 1295°F (700°C) on the W- UO_2 surface. The effects of post deposition heat treatment, 15 minutes at 3600°F in vacuo, on the fuel retention behavior of deposits produced at these conditions is illustrated in Figure 29. As seen previously, less porosity is observed in the clad of the heat treated sample after fuel retention testing than after testing the as deposited sample. Again, little porosity is evident in the clad layer that was deposited at 1295°F (700°C) adjacent to the W- UO_2 compact surface.

Figures 30 and 31 are photomicrographs of sections through fuel retention tested samples that had the surface exposed UO_2 removed from the W- UO_2 composite by etching for 30 minutes in HNO_3 prior to cladding at 895°F (480°C), 10:1 H_2/WF_6 ratio. The sample shown in Figure 30 was tested in H_2 at 4500°F (2480°C) in the as-clad condition. The sample shown in Figure 31 was heat treated at 3600°F (1980°C) for 15 minutes at 10^{-6} mm Hg prior to testing. Review of the two figures reveals that exposure to the fuel retention test environment has produced porosity in the cladding of both samples but to a lesser extent in the sample that was heat treated in vacuum prior to testing.

As previously discussed, trace quantities of zirconium were found in the surface layers of some W-20% UO_2 plates. To define the influence of this impurity, a sample which had 0.003" of material removed from one side by abrading was clad at 895°F (480°C), 10:1 H_2/WF_6 ratio and subsequently tested at 4500°F (2480°C) in flowing hydrogen for 2 hours. Photomicrographs of this sample after testing, Figure 32, indicate that essentially no difference exists in porosity formation and, fuel retention behavior between the two sides.

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FIGURE 26

Sample No. 56 after test at 4500°F (2480°C) in hydrogen for 2 hours.
Deposition parameters: 895°F (480°C), H_2/WF_6 -10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2 .

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FIGURE 27

Sample No. 56-1 after test at 4500°F (2480°C) in hydrogen for 2 hours which followed post-deposition heat treatment at 3600°F (1980°C) for 15 mins. at 10⁻⁶ mm Hg.

Deposition parameters: 895°F (480°C), H₂/WF₆ -10/1, 17 mm Hg.

Pretreatment: 15 mins. at 1600°F (870°C) in H₂.

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FIGURE 28

Sample No. 57 after test at 4500°F (2480°C) in hydrogen for 2 hours.
Deposition parameters: 1295°F (700°C), H_2/WF_6 -10/1, 17 mm Hg
followed by 895°F (480°C), H_2/WF_6 -10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2 .

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FIGURE 29

Sample No. 57-1 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
Sample was heat treated (after deposition) at 3600°F (1980°C) for 15 mins.
at 10⁻⁶ mm Hg prior to testing.

Deposition parameters: 1295°F (700°C), H₂/WF₆-10/1, 17 mm Hg
followed by 895°F (480°C), H₂/WF₆-10/1, 17 mm Hg.

Pretreatment: 15 mins. at 1600°F (870°C) in H₂.

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FIGURE 30

Sample No. 71 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
UO₂ removed from surface of compact by etching in HNO₃ for 30 mins.
prior to cladding.

Deposition parameters: 895°F (480°C), H₂/WF₆-10/1, 17 mm Hg.

Pretreatment: 15 mins. at 1600°F (870°C) in H₂.

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FIGURE 31

Sample No. 72 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
UO₂ was removed from compact by etching in HNO₃ prior to cladding.
Clad compact was heat treated at 3600°F (1980°C) for 15 mins. at 10⁻⁶ mm Hg
prior to testing.
Deposition parameters: 895°F (480°C), H₂/WF₆ -10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H₂.

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FIGURE 32

Sample No. 59 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
About 0.003" was abraded from one surface prior to cladding.
Deposition parameters: 895°F (480°C), H_2/WF_6 -10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2 .

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It has been observed that, although weight losses are comparable, larger pores are formed during fuel retention testing in tungsten claddings deposited on W- UO_2 composites received from NASA in Batch 2 than are formed in the clad on composites received in Batch 1. This effect, which has been found to be consistent regardless of clad deposition parameters or post deposition thermal treatment, is illustrated in Figures 33 and 34. Figure 33 is a clad Batch 2 compact after fuel retention testing. Figure 34 is a Batch 1 compact clad and tested under identical conditions. It is quite evident that the porosity in the cladding on the Batch 2 compact is considerably larger than the porosity seen in the Batch 1 compact. No explanation for this occurrence can be proffered at this time. It is curious to note that the as-received surface of the Batch 1 compacts was markedly discolored, as discussed previously, and that the UO_2 lattice was decidedly constricted whereas, the Batch 2 compacts were bright and clean with only slight UO_2 lattice constriction. As a first analysis, one would expect that the above porosity situation would be reversed, i.e., the Batch 2 compacts would behave better than the Batch 1 compacts.

From the weight loss data, it is evident that the formation of porosity in the vapor deposited tungsten cladding on W- UO_2 composites during single cycle fuel retention testing does not degrade the effectiveness of the cladding for precluding gross fuel losses. When multiple cycle tests are considered; however, it is conceivable that this porosity might seriously compromise the fuel retention capability of the cladding. It is strongly recommended, therefore, that additional work be directed toward eliminating this effect.

Testing of tungsten cladding on unfueled, recrystallized tungsten substrates at the fuel retention test conditions has resulted in the formation of porosity in the clad. This indicates that porosity formation is apparently a property of the cladding per se (perhaps WF_4 or WF_5), with only little effect being precipitated by the W- UO_2 composite during the test or during cladding. A photomicrograph of such a clad, plain tungsten sample after testing is shown in Figure 35. It is obvious that porosity formation is quite similar to that observed in high-temperature-tested, clad, fueled substrates.

Bend tests at 1000°F (540°C) have been run on clad W- UO_2 samples after testing at 4500°F (2480°C) in hydrogen for 2 hours. A photomicrograph of a section through the break in a bend tested sample is shown in Figure 36. Examination of the figure shows no signs of fracture at the clad-substrate interface. High temperature fuel retention testing has apparently not degraded the cladding bond.

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FIGURE 33

Cladding on NASA W-UO₂ compact from Batch 2 after
fuel retention testing.

Deposition parameters: 895°F (480°C), H₂/WF₆-10/1,
17 mm Hg.

Pretreatment: 15 mins. at 1600°F (870°C) in H₂.

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FIGURE 34

Cladding on NASA W-UO₂ compact from Batch 1 after fuel retention testing

Deposition parameters: 895°F (480°C), H₂/WF₆-10/1,
17 mm Hg.

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FIGURE 35

Two views of tungsten cladding on a sample of plain, recrystallized tungsten after testing at 4500°F (2480°C) in hydrogen for 2 hours. Deposition parameters and pretreatment: same as Figure 33.

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FIGURE 36

Photomicrograph of sample that was bent around a 0.025" radius at 1000° F (540° C) after testing at 4500° F (2480° C) in hydrogen for 2 hours.

CONCLUSIONS

1. The rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be varied in a predictable and reproducible manner by exercising control over the temperature, pressure, and gas flow rates at which the deposit is made. Deposition rate is most strongly dependent on temperature and pressure; longitudinal uniformity, on deposition rate versus gas flow rate. Both deposition rate and deposit uniformity over a 3-inch length are influenced by deposition chamber geometry. At constant WF_6 flow (cc/min.), deposition rate increases and uniformity is improved as the cross sectional area of the chamber is reduced.
2. The thickness of pyrolytic tungsten deposits can be readily controlled well within a total spread of 0.0005" in the 0.0005" to 0.001" range and to within 0.001" in the range 0.001" to 0.005".
3. The density of deposits made over wide ranges of parameters exceeds 98% of the theoretical density.
4. Deposits can be made to grow epitaxially from both tungsten and tungsten- UO_2 substrates with excellent adherence by pretreating the substrates in hydrogen at less than 15 mm Hg absolute and 1600°F (872°C) in the deposition chamber prior to coating to reduce surface oxides and provide a clean surface on which the deposit may nucleate.
5. Sectioning clad substrates with an abrasive disc cutter prior to metallographic preparation is an excellent, although somewhat crude, tool to evaluate deposit adherency. If the deposit is non-adherent, separation at the interface invariably occurs.
6. Currently available eddy current and pulse echo ultrasonic testing techniques are not sufficiently sensitive to detect non-adherent, mechanical bonding at the interface between the vapor deposited tungsten and tungsten substrate.
7. Although adherent, substrate nucleated deposits may be produced on W- UO_2 composites, the structure of the deposit over UO_2 particles that are exposed to the substrate surface is columnar and non-substrate nucleated.
8. Deposits produced on both unfueled, recrystallized tungsten and on W- UO_2 composites exhibit a high enough degree of adherency to survive bend tests at room temperature, 800°F (430°C), and 1000°F (540°C) around a 0.025" radius without separating at the substrate-clad interface.
9. The structure of tungsten deposits on W- UO_2 composites may be altered by recrystallization and bonding may be improved, as a result of grain growth across the interface, by post deposition heat treatment at 3600°F (1980°C) for 15 minutes in a vacuum of 10^{-6} mm of Hg.

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10. As revealed by fluorescent penetrant inspection, deposits produced over a wide range of deposition rates are free from surface defects and cracks.

11. Deposits produced on substrates directly heated by induction exhibit the same high degree of uniformity, adherency, and substrate nucleation as deposits produced on substrates heated radiantly in a hot chamber. It appears that basic technology developed with hot wall deposition systems may be equally applied to coating directly heated samples in cold wall systems with only minimal additional experimentation being required to establish optimum gas flow and deposit growth rates.

12. The microhardness of tungsten deposited from WF_6 averages 595 DPH and increases slightly with deposition temperature. Post deposition heat treatment at $3600^{\circ}F$ ($198^{\circ}C$) for 15 minutes at 10^{-6} mm of Hg decreases the average hardness to about 465 DPH.

13. With the exception of Cu, C, and F, the level of 26 elements sought in vapor deposited tungsten is less than 10 ppm each. Copper, carbon, and fluorine levels are each less than 20 ppm, 33 ppm and 20 ppm respectively.

14. Tungsten deposited from WF_6 vapor on W-20% UO_2 composites effectively and consistently restricts fuel loss from the composites to less than 0.15 mg/cm^2 (0.21% of contained UO_2) for times up to 2 hours at $4500^{\circ}F$ ($2480^{\circ}C$) in flowing hydrogen.

15. Vapor deposited coatings on W-20% UO_2 exhibit micro porosity after being tested at $4500^{\circ}F$ ($2480^{\circ}C$) in hydrogen for 2 hours, the degree of which is dependent upon deposition parameters and post deposition heat treatment history.

16. Post deposition heat treatment of tungsten clad W- UO_2 composites ($3600^{\circ}F$ ($198^{\circ}C$) at 10^{-6} mm of Hg for 15 minutes) significantly reduces the formation of porosity in the clad during 2 hour high temperature testing at $4500^{\circ}F$ ($2480^{\circ}C$) in hydrogen.

17. Thin layers of tungsten deposited on W- UO_2 composite surfaces at $1295^{\circ}F$ ($700^{\circ}C$) prior to depositing a thicker, more easily controlled layer at $896^{\circ}F$ ($480^{\circ}C$) exhibit virtually no porosity after the high temperature fuel retention test.

18. Porosity in the pyrolytic tungsten cladding after high temperature fuel retention testing appears in the greatest number and of largest diameter adjacent to areas in the composite where UO_2 particle concentrations are heaviest.

19. Removal of UO_2 particles exposed to the surface of the W- UO_2 composites by dissolution with HNO_3 prior to cladding deposition offers no advantage to improving fuel retention performance in single cycle tests at $4500^{\circ}F$ ($2480^{\circ}C$) in hydrogen.

20. Small thinly coated or even uncoated areas effected on one edge of each W- UO_2 composite by 12 mil diameter tungsten wire used to support the composites in the deposition

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chamber do not compromise the ability of the clad to minimize high temperature fuel losses.

21. Trace quantities of zirconium detected in the surface of as-rolled W-UO₂ composites do not significantly degrade the vapor deposited tungsten cladding during single cycle high temperature fuel retention testing at 4500°F (2480°C) in hydrogen for 2 hours.

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RECOMMENDATIONS

Recommendations for Task II

The production of a large number of samples, using parameters developed under Task I, to more firmly establish the effectiveness of vapor deposited tungsten coatings in minimizing fuel losses from W-UO₂ composites when exposed to hydrogen at 4500°F (2480°C) is the prime objective of Task II. Being such, it is obviously advisable that these samples be produced via a process that is as optimized as present knowledge permits. Development work under Task I has revealed that an, as yet undefined, relationship exists between the degree of porosity that is formed in the cladding during single cycle testing at 4500°F (2480°C) in hydrogen and the temperature at which the cladding was deposited. A similar relationship exists between porosity formation and post-deposition thermal treatments. Although this porosity does not degrade the fuel retention ability of the cladding under 2 hour continuous exposure to hydrogen at the test temperature, it is conceivable the deleterious effects might develop in multi-cycle tests or in tests at higher temperatures. It is, therefore, recommended that the following additional work be done, on at least a minimum effort basis within the scope of the current contract, to optimize the process prior to producing samples for NASA-Lewis.

1. Evaluate the effects of higher deposition temperatures on the reduction of pore formation during the fuel retention test.
2. Investigate the relationship between post deposition heat treatment time and temperature and the fuel retention test porosity formation in cladding deposited at both high and low deposition temperatures.

Anticipating that porosity formation will be significantly reduced in cladding deposited at higher temperatures, it is further recommended that additional efforts be concomitantly directed toward resolving the problem of deposit non-uniformity and control that might occur at high deposition rates due to depletion of WF₆ from the gas stream. Past experience suggests that this can be best accomplished in an induction heated, cold wall system using high WF₆ flow rates and an internal manifold or baffle system to assure uniform WF₆ delivery to all parts of the heated sample. The maximum Task II sample size of 7" dictates that uniform temperature be achieved over at least this length. In the interest of high production rates due to the large number of samples involved, it is desirable that the system be equipped to process multiple samples without opening or cooling the system.

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Recommendations for the Future

Little information is presently available that relates the influence of cladding impurities to the elevated temperature fuel retention performance of clad W-UO₂ composites. Since it is desirable that the cladding process be finalized as a reliable, reproducible production method at the earliest possible date, it is recommended that additional experimental work on the control of impurities be initiated. This work should include defining all elements that might affect elevated temperature fuel retention performance by controlling the source of these impurities in both system construction materials and in processing gases (H₂, Ar, and WF₆).

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APPENDIX I

Determination of Oxygen-Uranium Ratio in Surface UO_2 of Rolled Plates of W-20 v/o UO_2

X-ray diffraction measurements were made on the exposed surface UO_2 phase of the W- UO_2 composites to test for the presence of excess oxygen. A reduced lattice parameter of the UO_2 indicates that the oxygen-uranium ratio is greater than 2 to 1.

Measurements were made on a diffractometer with a copper target diffraction tube to measure the 2θ angle in the region from 26° to 60° . Particular attention was paid to the (311) UO_2 peak occurring between 55° and 57° . As a standardizing method to determine the UO_2 composition, a plate was sectioned and 4 or 5 pieces were mounted in plastic metallographic mounting material with the cut edges side by side. A diffractometer trace was taken of this composite surface to determine the composition of the internal UO_2 . This trace shows the (311) d-spacing to have a value of 1.6515 (2θ angle of 55.64°) indicating a nearly normal lattice parameter of 5.47 Å. The external surfaces of all the rolled samples were then scanned and the resultant UO_2 d-values compared with that obtained for the internal UO_2 particles. The tungsten peaks in all cases were used as a standard check of goniometer alignment.

The diffractometer patterns from the surface UO_2 of all samples showed the same cubic structure as the interior UO_2 , but the calculated lattice parameters for the surface particles were smaller than that obtained for the interior UO_2 particles indicating excess oxygen present in the lattice of surface UO_2 . It should also be mentioned that it is possible for other contaminants to similarly reduce the lattice parameters as indicated in the body of the report.

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