URANIUM OXIDE FUEL FOR NUCLEAR THERMIONIC CONVERTERS

MACTED

L. N. Grossman*, R. A. Ekvall*, and H. W. Hill*

Introduction. Nuclear thermionic power conversion requires emitter temperatures of the order of 1600°C or higher. Both power density and efficiency increase with emitter temperature; values of 21.6 W/cm² at 21% efficiency at 1877°C have been achieved in laboratory tests.⁽¹⁾ Phenomena accompanying high emitter temperatures have presented the principal technological problems in the development of nuclear thermionic converters. The objective of this study has been to demonstrate the suitability of UO₂ as a nuclear fuel when it is in contact with tungsten, molybdenum, and W-25% Re thermionic emitters.

Preliminary choices of fuel materials for use with metallic emitters were:⁽²⁾ UO₂-W; UO₂-Mo; UC-W; (U, Zr)C-W; (U, Zr)C-Mo; and UC_{1+x}-W. At the General Electric Company, primary emphasis has been on the development of UO₂ fuel. This choice resulted from (a) considerable experience with UO₂ fuel in power reactors⁽³⁾ and (b) early experimentation⁽⁴⁾ with UC-W and UO₂-W which showed that gross interaction could occur in the UC-W system near 2000°C, while no interactions were observed between UO₂ and tungsten to at least 2300°C. Further development of (U, Zr)C and other carbide fuels has been carried out at the Los Alamos Scientific Laboratory and at the John Jay Hopkins Laboratory of General Dynamics Corporation^(5,6,7) Horner, Weinberg, and Yang⁽⁷⁾ showed that only tungsten was unequivocally suitable as a cladding material for carbide fuel at 1800°C. It will be shown that based on the furnace tests reported herein, tungsten, molybdenum, and W-25% Re are suitable with UO₂ fuel in the temperature range of thermionic application and that alloys based on tungsten, molybdenum, or rhenium are potentially useful.

Materials Selection. The cladding materials were chosen on the basis of several important factors: 1. Electron emission characteristics in cesium converters; 2. Physicochemical properties, e.g., low vapor pressure and high melting point; 3. Compatibility with the nuclear fuel (urania) at high temperatures based on thermodynamic considerations; 4. High temperature strength and low creep rates; 5. Fabricability and availability; 6. Neutron cross section, i.e., core design consideration. The first and second requirements were easily met by metals such as tungsten, molybdenum, tantalum and rhenium. Nuclear cross section considerations could be satisfied with molybdenum for thermal reactors and by molybdenum, tungsten, and tungsten-base alloys for the fast reactor systems. Vapor pressure (vaporization loss in vacuum) limits the application of molybdenum to 1700°C or lower. No serious vaporization temperature limit exists for tungsten or rhenium up to 2300°C, or for tantalum up to 2200°C. When the materials were chosen, tantalum was considered first because of its ease of fabrication, but was discarded because of its relatively poor high-temperature strength and high creep rates. Mechanical stability is critical because the 10-mil (or smaller) spacing between the electron emitter and the collector must be maintained. It was assumed the tungsten fabrication problems could be solved. Experience has shown this assumption to be correct. Strength and fabricability of molybdenum and rhenium were acceptable. The major unproved criterion was the compatibility and interaction of urania with the emitter materials.

* General Electric Company, Atomic Power Equipment Department, Vallecitos Atomic Laboratory, Pleasanton, California, U.S.A. This work was supported by the U. S. Atomic Energy Commission and the National Aeronautics and Space Administration.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

It can be shown from existing thermodynamics data that no reaction is expected between stoichiometric uranium dioxide and tungsten, rhenium, and molybdenum. The same criteria applied to tantalum and niobium indicated that these materials may react; therefore, they were not chosen for investigation.

The thermionic application requirements were for 10,000-hour reactor operation at fuel-cladding temperatures of approximately 1700°C, with possible increases in time and temperature requirements. Research was directed toward long-term, high-temperature compatibility and thermal cycling tests of urania with tungsten, tungsten-25% rhenium, and molybdenum.

Material and Experimental Procedures. A. Characterization of Starting Materials. Stoichiometric UO_2 pellets were fabricated by cold pressing, then sintering. Data on the spectrographic analysis and the ratio of atomic percent oxygen to atomic percent uranium (O-to-U) of a typical sintered pellet of stoichiometric UO_2 are given in Table I.

Two techniques were used for preparing hyperstoichiometric urania pellets. In the first method, UO_2 and U_3O_8 powders were blended and sintered at temperatures up to 1550°C in argon; e. g., low density (84% T.D.) urania pellets with an O-to-U ratio of 2.185 were prepared from a blend of 80 wt % $\text{UO}_{2.041}$ and 20 wt % $\text{UO}_{2.67}$ by sintering in argon at 1450°C, the samples were held at temperature for two hours. X-ray diffraction analyses showed the presence of U_4O_9 and UO_{2+x} phases in the sintered pellets. In the second method, sintering in steam and reducing in hydrogen-helium atmospheres were used to produce hyperstoichiometric urania pellets of higher densities and controlled O-to-U ratios.

Exposure of pressed UO_2 compacts to flowing steam at 1500°C has resulted in rapid densification and oxidation to $\text{UO}_{2.185} \pm 0.005$. Firing in 94% He-6% H_2 at 1150°C permitted a controlled reduction of the pellets. The $\text{UO}_{2.085}$ pellets with densities of 92% T.D. were obtained by sintering in steam for 1/2 hour and then in argon for 1/2 hour at 1500°C, cooling to 1150°C in argon, and reducing in 94% He-6% H_2 at 1150°C for 2 hours. Hyperstoichiometric urania pellets produced by each of the foregoing methods have been uniform within ± 0.015 in O-to-U ratio from the surface to the center.

B. Specimen Fabrication. A test specimen consisted of a UO_2 pellet encapsulated in a thin walled (~ 0.020 -inch) cylindrical refractory metal container, approximately 0.450-inch diameter by 0.5-to 1.0-inch long. The room temperature UO_2 pellet dimensions were selected so that expansion at test temperature would cause the pellet to contact the container. The containers were fabricated from a given refractory metal by welding end caps on each end of a tubular section using a tungsten inert gas (TIG) process inside a clean argon glove box. Vented and unvented containers were prepared which were identical except for a ~ 0.020 -inch-diameter vent hole centrally located in one end cap of each of the vented containers.

Typical chemical analyses of the as-received refractory metals are given in Table I. For brevity, only the composition of the tube of a given refractory metal is shown, where corresponding rod compositions were similar.

The container components were fabricated by cutting the tubing to length with a cut-off wheel; the end caps were machined from bar stock. After encapsulation of the UO_2 in the containers by welding, all samples were macroscopically examined, weighed, and measured. Unvented samples were leak-checked with a helium mass spectrometer leak detector.

TABLE I
CHEMICAL ANALYSIS OF TYPICAL STARTING MATERIALS

Element	Finished UO ₂ Pellet (O:U Ratio 2.007±0.005)	W ¹	W ²	Mo ³	W 25% Re ⁴	Analytical Technique
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
Re	n.d.*	n.d.		n.d.	24.7%	X-ray fluorescence
C	13	50	< 10	n.d.	< 10	Conductometric
N	n.d.	23	20	7	10	Kjeldahl
O		50	49	n.d.	15	Inert gas fusion
Ag	< 0.1	1	n.d.	n.d.	n.d.	Emission spectroscopy
Al	< 10	< 10	< 10	20	< 10	"
B	< 0.2	10	n.d.	n.d.	n.d.	"
Bi	< 1	n.d.	n.d.	n.d.	n.d.	"
Ca	< 25	1	n.d.	20	n.d.	"
Cd	< 1	< 100	n.d.	n.d.	< 100	"
Co	< 1	10	n.d.	20	n.d.	"
Cr	< 10	< 10	< 10	100	< 10	"
Cu	< 1	1	< 10	100	< 10	"
F	< 5	n.d.	n.d.	n.d.	n.d.	"
Fe	25	10	< 10	200	< 10	"
Hf	n.d.	n.d.	< 50	n.d.	< 50	"
Mg	2	1	n.d.	4	n.d.	"
Mn	1	1	n.d.	2	n.d.	"
Mo	< 3	< 10	< 10		90	"
Na	< 35	n.d.	n.d.	n.d.	n.d.	"
Nb	n.d.	< 100	< 100	n.d.	n.d.	"
Ni	15	10	< 10	10	< 10	"
Pb	< 1	50	n.d.	n.d.	n.d.	"
Si	15	100	< 10	200	< 10	"
Sn	< 1	< 50	n.d.	100	n.d.	"
Ta	n.d.	n.d.	< 250	n.d.	< 250	"
Ti	n.d.	< 10	< 10	n.d.	< 10	"
U		< 0.1	n.d.	< 2	< 2	Mass spectrometry
V	< 15	1	n.d.	n.d.	n.d.	Emission spectroscopy
W	n.d.			< 100	75.3%	"
Zn	< 10	n.d.	n.d.	n.d.	n.d.	"
Zr	n.d.	< 10	< 25	n.d.	n.d.	"

* n.d. = no determination.

1. Vapor deposited W tubing supplied by San Fernando Laboratories.
2. Sintered and swaged rod from General Electric Company (Type-218).
3. Sintered and drawn tubing from Cleveland Tungsten Company.
4. Sintered tube from Hoskins Mfg. Company.

C. Test Program. Depending on the desired test environment, samples to be isothermally tested were either placed directly into a vacuum test furnace or were enclosed in a tantalum cesium test chamber (as shown) which was in turn placed in a two-zone vacuum furnace. Furnace temperatures were controlled to $\pm 1\%$. After initial heat-up, pressure in the vacuum furnace was between 10^{-7} and 10^{-6} torr.

Thermal cycling tests were performed in an induction-heated vacuum (10^{-6} to 10^{-5} torr) chamber. Temperatures were measured with calibrated optical pyrometers to within $\pm 1\%$.

The isothermal and thermal cycling test programs are listed in Tables II and III, respectively. For brevity, isothermal tests of W- UO_2 and Mo- UO_2 less than 3000 hours and of W-25% Re- UO_2 less than 1000 hours are not listed. Materials of samples 5, 7, 10, and 12 were obtained from different sources than those shown in Table I. Tests of these samples are listed, however, to indicate the full scope of the program. Excess oxygen sample MO-17 was heated stepwise from 750 to 1700°C in 100 degree intervals with a holding period of approximately 3 hours at each temperature.

For extended compatibility tests in cesium, a surveillance program was established. At 1000-hour intervals, the tantalum chambers were checked for leaks. If a leak formed, the compatibility specimens were transferred to new chambers. For small leaks, the cesium loss rate was slow enough to ensure that liquid cesium would be in the well. The capsules were measured, weighed, and leak-checked whenever a tantalum chamber was changed (typical chamber life was 2000 hours at 1700 and 1900°C). The tungsten furnace elements were redesigned to extend their life to about 5000 hours at 1900°C (when sagging shorted them). The diffusion-pumped vacuum systems which were equipped with molecular sieve traps presented no maintenance problems. The six vacuum furnaces used in these tests have logged about 50,000 hours and are still in good condition.

D. Post-test Evaluation. After thermal testing, each sample was macroscopically examined for surface defects, measured, and weighed. Each unvented sample was helium leak-checked. Samples were then sectioned longitudinally, polished and/or etched, and microscopically examined. Where appropriate, further sample analysis was performed by electron beam microprobe, mass spectrometry, wet chemistry, emission spectroscopy, x-ray diffractometry, and x-ray fluorescence. Mass balance was obtained on vented capsules tested in cesium, by acid leaching the tantalum chamber and analyzing for uranium.

Experimental Results. A. Compatibility Under Isothermal Conditions. The measure of compatibility between the fuel and the cladding was established principally by post-test metallographic examination. These examinations failed to uncover new phases of any materials other than UO_2 and the cladding materials, when stoichiometric UO_2 was the starting material. The examinations were supplemented by microprobe studies of the interfaces between the fuel and cladding. No detectable composition gradients were observed. Three subtle changes in the fuel-emitter couples have been observed after testing: (1) small amount ($<0.1\%$) of uranium metal is generally found in the UO_2 ; (2) small amounts ($<0.05\%$) of uranium are found in the cladding material; and (3) small amounts ($<0.1\%$) of cladding material are sometimes observed in the UO_2 .

The first effect has been seen in most compatibility specimens exposed for over 500 hours to above 1700°C. The uranium inclusions are both at grain boundaries and

TABLE II
ISOTHERMAL TEST PROGRAM

<u>Material</u>	<u>Code</u>	<u>Vented</u>	<u>Test Temp (°C)</u>	<u>Target Test Time (Hours)</u>	<u>Furnace Exposure Status</u>	<u>Atmos</u>	<u>Evaluation Complete</u>
UO ₂ -W	W-5	No	1900	10,000	Complete	Cesium	No
UO ₂ -W	W-6	Yes	1900	10,000	Complete	Cesium	No
UO ₂ -Mo	M-7	No	1700	10,000	Terminated 5993 hours	Cesium	Yes
UO ₂ -Mo	M-8	Yes	1700	10,000	Complete	Cesium	No
UO ₂ -Mo	MO-18	No	1700	10,000	Terminated 6439 hours	Vacuum	Yes
UO ₂ -W	WO-14	No	1900	10,000	Terminated 3919 hours	Vacuum	Yes
UO ₂ -W	WO-11	No	1900	10,000	Terminated 7395 hours	Vacuum	Yes
UO ₂ -W	WO-12	No	1900	10,000	Complete	Vacuum	Yes
UO ₂ -W25%Re	C	Yes	1800	1,000	Complete	Cesium	Yes
UO ₂ -W25%Re	G	Yes	2000	1,000	Complete	Cesium	Yes
UO ₂ -W25%Re	J	Yes	1800	1,000)	Complete	Cesium	Yes
			2000	1,000)			
UO ₂ -W25%Re	I	Yes	2000	2,000	Complete	Cesium	Yes
UO ₂ -W25%Re	5	Yes	1800	3,000	Complete	Cesium	No
UO ₂ -W25%Re	7	Yes	1800	5,000	4235 hours	Cesium	No
UO ₂ -W25%Re	10	Yes	2000	3,000	Complete	Cesium	No
UO ₂ -W25%Re	12	Yes	2200	1,000	Complete	Cesium	No
UO ₂ .085W25%Re	L	No	2000	500	Complete	Vacuum	Yes
UO ₂ .185Mo	MO-13	No	1900	100	Complete	Vacuum	Yes
UO ₂ .185Mo	MO-16	No	1900	112	Complete	Vacuum	Yes
UO ₂ .185Mo	MO-17	No	1700	Stepwise	Complete	Vacuum	Yes

TABLE III
THERMAL CYCLING TEST PROGRAM

<u>Cycle Mode</u>	<u>Materials</u>	<u>Code</u>	<u>Vented</u>	<u>Max Cycle Temp (°C)</u>	<u>Time at Temp (min)</u>	<u>Min Cycle Temp (°C)</u>	<u>Time at Temp (min)</u>	<u>Period of Cycle (min)</u>	<u>No. of Cycles</u>
I	W-UO ₂	WO-15	No)	2000	3 h	1800	21 h	24 h	30
	W-UO ₂	WO-16	Yes)						
	Mo-UO ₂	MO-21	No)						
	Mo-UO ₂	MO-22	Yes)						
II	W-UO ₂	WO-17	No)	2000	2	1800	8	10	50
	W-UO ₂	WO-18	Yes)						
	Mo-UO ₂	MO-23	No)						
	Mo-UO ₂	MO-24	Yes)						
III	W25%Re-UO ₂	L	Yes	1800	10	725	5	15	50
IV	W25%Re-UO ₂	M	Yes	2000	10	725	5	15	50
V	W25%Re-UO ₂	N	Yes	2200	5	1600	5	10	50

within grains. The amount of uranium has been too small to measure accurately. The O-to-U ratio of the urania changes slightly (1.996 ± 0.004) from the stoichiometric composition. The uranium inclusions appear randomly throughout the specimens.

The appearance of uranium in the cladding has taken two forms. Small inclusions of UO_2 in the immediate vicinity of the fuel-cladding interface have been observed. The number of such inclusions is small and they are often localized near the clad- UO_2 interface at one end of the capsule in the metal-grain boundaries. The W-Re specimens I and J appeared to have more UO_2 inclusions than the other specimens. However, the size (<10 microns) and number of these inclusions was too small for accurate measurements of the amount present. The bulk uranium content of the cladding has also increased during the isothermal exposures. The tungsten wall of specimen WO-12 contained 76 ppm uranium and the lid contained 198 ppm uranium after testing. Further analyses for uranium content of the claddings are in progress. Small inclusions of cladding metal in the UO_2 have been observed occasionally. The inclusions are found in grain boundaries and in pores. No correlation with test conditions or test materials has been found.

The effect of hyperstoichiometry upon the compatibility of urania and molybdenum was investigated on specimens MO-13, MO-16, and MO-17 (Table II). The $\text{UO}_{2.185}$ pellets were sealed in Mo capsules forming a closed system. Initial testing was performed isothermally at 1900°C to determine the extent and mechanism of interaction between the $\text{UO}_{2.185}$ and Mo. Microscopic examination of MO-13 (exposed for 100 hours at 1900°C in vacuum of 2×10^{-5} torr) showed that a gross reaction had occurred in the system. Molybdenum moved from the cladding wall into the interior of the hyperstoichiometric urania pellet and deposited in the urania grain boundaries. X-ray diffraction analyses of the fuel pellet after the exposure revealed only two phases, $\text{UO}_{2.008}$ and molybdenum. Weight loss data also verified that the excess oxygen had left the system. Since the capsule was leaktight after testing, it is concluded that the oxygen diffused through the molybdenum cladding.

To gain an understanding of the mechanism of the UO_{2+x} -Mo interaction which was detected in the 100-hour exposure, sample MO-16 was exposed for 1/2 hour in vacuum at 1900°C . Weight loss measurements indicated that most of the oxygen in excess of that contained in $\text{UO}_{2.00}$ + Mo had again left the system. X-ray diffraction analyses indicated $\text{UO}_{2.018}$, molybdenum, and a minor amount of an unidentified third phase. An examination of the microstructure revealed UO_2 , molybdenum, and an additional phase which appeared similar to a eutectic reaction. This eutectic phase consisted of a dispersion of metallic particles less than 2 microns in diameter in a non-metallic matrix. The eutectic phase was analyzed by electron microprobe and contained about 55 wt % Mo.

A third $\text{UO}_{2.185}$ pellet, clad in molybdenum (specimen MO-17), was exposed to lower temperatures. The sample was held for 3 hours at successively higher temperatures as shown in Table IV. No significant weight loss was detected until the 1400°C exposure was completed. The rate of oxygen diffusion through the 0.020-inch molybdenum cladding increased markedly at 1600 and 1700°C . The high-temperature exposures of the samples were terminated before all the excess oxygen had left the system. The sample was analyzed by x-ray diffraction and metallographic techniques after the 1700°C exposure was completed. Based on the weight loss, the $\text{UO}_{2.185}$ should have been reduced to $\text{UO}_{2.077}$, however, measurement of the lattice perimeter of the UO_{2+x} phase indicated that the O-to-U ratio was 2.015. An additional non-metallic phase not detected in the two previous samples was detected on the inside wall of the molybdenum cladding. This phase was examined by electron microprobe analysis and found to contain about 70 wt % Mo and <1 wt % U (the balance was presumably oxygen). It was assumed to be UO_2 , therefore, at the low-temperature, oxygen in excess of $\text{UO}_{2.00}$ apparently left the UO_2 and reacted with molybdenum to form MoO_2 . In this sample, which had been treated only to 1700°C , there was no evidence of molybdenum within the UO_2 pellet nor of gross interaction between the UO_{2+x} and molybdenum.

Extensive interaction occurred between the $\text{UO}_{2.085} \pm 0.005$ and the W-26% Re cladding of sample L. A hole formed in the capsule wall at the bottom corner. The hole

was apparently produced by a combination of internal pressure (all samples were sealed in an argon atmosphere) and liquid attack on the cladding. It was evident the specimen had bulged during testing.

TABLE IV
RATE OF WEIGHT LOSS OF SAMPLE MO-17

<u>Exposure</u> <u>Temp. °C</u>	<u>Time at</u> <u>Temperature (hours)</u>	<u>Cumulative</u> <u>Exposure (hours)</u>	<u>Cumulative</u> <u>Oxygen Loss*</u>
750	3	3	< 0.1
900	3	6	< 0.1
1000	3	9	0.14
1200	3	12	0.23
1400	3	15	0.79
1500	3	18	4.98
1600	3	21	15.59
1700	3	24	47.51

* Expressed as percent of total oxygen present in excess of $\text{UO}_{2.00}$ in hyper-stoichiometric $\text{UO}_{2.185}$.

B. Thermally Cycled Specimens. The effects of fast and slow thermal cycles were evaluated on the specimens shown in Table III. Weight loss rates were obtained for the vented specimens to find whether enhanced evaporation resulted from cycling. A comparison of observed weight loss after cycling to the equilibrium weight loss expected⁽⁸⁾ in vacuum from evaporation of the UO_2 for some samples is shown:

<u>Specimen Code</u>	<u>WO-16</u>	<u>MO-22</u>	<u>L</u>	<u>N</u>
Observed (gm/cm^2 cycle)	1×10^{-3}	1×10^{-3}	5×10^{-4}	0.12
Theoretical (gm/cm^2 cycle)	2×10^{-3}	2×10^{-3}	5×10^{-4}	0.10

Weight loss of the cladding is ignored in the table. After cycling, the specimen had not changed in exterior dimensions and no exterior anomalies were observed. Helium leak-checking confirmed that the non-vented specimens had remained impervious to helium. Microstructural examination showed no gross interaction effects nor any features not seen in the isothermally treated specimens. Uranium inclusions in the UO_2 were observed although no trends in the uranium distribution could be seen. The amount of uranium in the tungsten- and molybdenum-clad specimens did show a trend, although the amounts were too small to measure quantitatively. The amount of uranium was greater in the vented molybdenum and tungsten specimens than in their non-vented counterparts; the amount of uranium was greater in the molybdenum specimens than in their tungsten counterparts.

The amount of uranium dissolved in the cladding material was measured for the tungsten- and molybdenum-clad specimens. The results are:

<u>Specimen</u>	<u>WO-15</u>	<u>WO-16</u>	<u>WO-17</u>	<u>WO-18</u>	<u>MO-21</u>	<u>MO-22</u>	<u>MO-23</u>	<u>MO-24</u>
Uranium (ppm)	21.5	8.6	3.7	1.1	215.3	9.6	126.9	80.0

The O-to-U ratio of the UO_2 phase of the specimens shown above was 2.002 ± 0.005 in all cases. The starting metals contained <1 ppm uranium in all cases.

C. Vaporization of UO_2 in Cesium Vapor. Weight loss measurements on vented tungsten- and molybdenum-clad specimens from the isothermal compatibility tests conducted in a cesium environment have yielded qualitative data on the evaporation of UO_2 . An initial weight loss rate much higher than the theoretical vacuum value is observed. The rate decreases rapidly and levels after about 100 hours (above 1700°C) have elapsed. The final weight loss rate was about 2 orders of magnitude below the value in vacuum. The geometry of the capsules approximates evaporation into a semi-infinite cover gas.

The effect of cesium cover gas on suppressing evaporation of molybdenum was demonstrated with specimens M-7 and MO-18. Both were exposed for about 6000 hours at 1700°C. No detectable thinning of the clad occurred for specimen M-7 which was tested in 4 torr cesium for 5993 hours. Specimen MO-18 ruptured after 6439 hours in vacuum due to thinning of the molybdenum by evaporation. The cladding decreased from the initial 0.020-inch thickness to an average thickness of 0.015 inch. The clad was breached presumably by the argon pressure (about 2 atmospheres) sealed inside.

Summary and Discussion. A. Long Term Compatibility Specimens Containing Stoichiometric UO₂. Observations made of the urania after testing were: (1) Densification and grain growth, (2) Uranium inclusions in the UO₂ matrix (<0.1%), (3) Cladding metal in the UO₂ (<0.1%), (4) No reaction with the clads, (5) No reaction with cesium vapor, and (6) Suppression of UO₂ evaporation by cesium vapor.

Grain growth of the UO₂ was not exceptional; the grain size followed Hausner's (9) observations for a closed system at 1900°C. The urania was close to theoretical density after testing. Uranium inclusions in the UO₂ are consistent with the phase diagram for U-UO₂ at high temperatures. (10) The hyperstoichiometric phase UO_{2-x} which exists at the test temperature disassociates on cooling to form stoichiometric UO₂ and metallic uranium:

The elemental uranium is most often observed at free surfaces; when rapidly cooled, uranium is also found as very small (~2μ) precipitates within grains. The presence of cladding metal in the UO₂ has been noted for some specimens but not for others. This effect is tentatively attributed to vapor (or liquid) transport of oxides formed on initial heating from excess oxygen in the fuel or from oxygen on the clad. No differences in behavior of the fuel were observed in vented specimens compared to the non-vented capsules. No effect attributable to cesium was observed except for suppression of vaporization of the urania. A suppression factor of 100 over vacuum sublimation rates was noted at 1700 and 1900°C under the conditions described.

Observations on the clad materials were: (1) Grain growth, (2) Chemical compatibility with UO₂, (3) Small compositional changes and UO₂ inclusions, (4) Evaporation suppression by cesium vapor, and (5) No interaction with cesium. Grain growth for non-vented specimens was observed to be greater than for vented specimens. The molybdenum-clad UO_{2+x} developed very large grains (larger than the wall thickness). Local areas of unusually large grains were also observed in clads of stoichiometric pellets. The variations in grain size have been found to be associated with oxygen diffusion through the cladding. The most stable grain structure was exhibited by tungsten in Table I. Uranium oxide inclusions in grain boundaries of the clad are attributed to two sources; (a) local areas of excess oxygen can cause reaction with the clad as is discussed below, and (b) uranium metal formed during cooling of UO_{2-x} can penetrate clad grain boundaries and then reoxidize when the specimen is reheated. The appearance of uranium in solution in the clad is also a result of uranium precipitation from UO_{2-x} at the fuel-clad interface on cooling. Cesium suppression of molybdenum evaporation is at least a hundredfold as shown by the comparison of specimens MO-18 and M-7. The evaporation in vacuum was about 0.005 inch as compared to the expected value⁽¹¹⁾ of 0.0013 inch at 1700°C. This discrepancy could be accounted for by a temperature error of 40°C.

B. Excess Oxygen Considerations for the Specification of UO₂. The experimental data resulting from the interaction of hyperstoichiometric UO₂ with molybdenum is consistent with the reduction of UO_{2+x} by molybdenum to form MoO₃(g, l) or MoO₂(s, l). Data^(12, 13) on the partial molar free energy of oxygen in UO_{2+x} have been extrapolated to the temperatures of interest in thermionics and compared to the free energy of oxygen in molybdenum oxides.^(14, 15) Virtually all oxygen in excess of the stoichiometric composition will interact with the cladding. In establishing a criterion for limiting the excess oxygen allowable in the fuel, a certain arbitrariness exists. One criterion could be to specify that fraction of the cladding which can be sacrificed by oxidation. Let us say that a uniform layer 0.0001 inch thick is tolerable; that about 10⁻⁴ mole excess oxygen is tolerable in a 1-cm-diameter x 2-cm-long fuel

element and corresponds to an O-to-U ratio of 2.003 in 15 grams of UO_2 . Thus, a specification for UO_2 for use in a molybdenum emitter is that the O-to-U ratio be less than, or equal to, 2.003. At thermionic temperatures ($T_E > 1500^\circ\text{C}$), the excess oxygen will eventually be transported through the emitter and will enter the inter-electrode space. At low oxygen concentrations, the excess oxygen will leave the emitter as O or O_2 and will be scavenged by other converter materials (e.g., niobium anode, molybdenum anode, and liquid cesium). Tungsten, rhenium, and W-Re-Mo alloys for UO_2 fuel cladding are subject to the same analysis given for molybdenum. Specimen L is an example of the excess oxygen reaction in W-26% Re alloy. Here, rapid heating caused a buildup of W-Re trioxide pressure inside the capsule. A hole appeared in an area weakened by liquid oxide attack on the cladding. The excess oxygen eventually left the system; therefore, only stoichiometric UO_2 and W-26% Re were present after the test.

C. Effects of Thermal Cycling. Sufficient evidence has been published on the high temperature stability of UO_2 to cause concern over its behavior under thermal cycling. Rothwell⁽¹⁶⁾ and Anderson⁽¹⁷⁾ were early observers of evidence supporting the existence of hypostoichiometric UO_2 . More recently, Kaznoff⁽¹⁸⁾ has observed enhanced diffusion of uranium through molybdenum and tungsten after thermal cycling. The experiments described here have shown no effects harmful to the operation of a thermionic converter. However, the relative amount of uranium observed in the various cycled specimens indicates that equilibrium probably had not been obtained. The results of this study should be extrapolated with caution to more cycles or to other cycling rates.

Conclusions. The results of an extensive furnace test program demonstrate that tungsten (at 1900°C), molybdenum (at 1700°C), and tungsten-25% rhenium (at 2000°C) are suitable candidate emitter cladding materials for nuclear thermionic energy conversion. Compatibility is maintained, under the test conditions described, for periods of thousands of hours. For molybdenum and tungsten, 10,000-hour testing has been completed with no harmful effects observed. Cesium vapor at 4 torr suppresses fuel and clad evaporation. Fuel stoichiometry is an important variable to control; fabrication and handling procedures to control stoichiometry of the fuel are well established.

Acknowledgment. The assistance of J. G. Wilson, J. E. Silva, J. O. Hegland, and C. M. Berry in conducting the experimental work is gratefully acknowledged. The continued interest and valuable reviews supplied by A. N. Holden, M. J. Sanderson, and A. I. Kaznoff were very helpful.

REFERENCES

1. Wilson, V. C. and Lawrence, J., High Performance Thermionic Converters, General Electric Research Lab Report 65-RL-3965E, June, 1965.
2. Grossman, L. N., Kaznoff, A. I., and Stephas, P., "Structural and Emitter Materials for Nuclear Thermionic Converters," in Metallurgy of Semiconductor Materials, J. B. Schroeder, Ed., Interscience Publishers, N. Y. (1962).
3. Belle, J., Ed., "Uranium Dioxide: Properties and Nuclear Applications," U. S. Government Printing Office, Washington, D. C. (1961); Uranium Ceramic Data Manual, compiled by B. J. Seddon, UKAEA, Risley, Warrington, Lancashire (1960). Available from H. M. Stationery Office; Kaznoff, A. I., Weidenbaum, B., and Sanderson, M. J., "Properties of Uranium Dioxide," in Progress in Ceramic Science, V. 4, J. E. Burke, Ed., MacMillan Publishing Co., N. Y. (1965).
4. Metallurgy and Ceramics Staff, General Electric Company, Vallecitos Atomic Laboratory, Quarterly Reports GEAP-3881 (January 1962) and GEAP-3821 (October 1961).

5. Yang, L., Weinberg, A.F., and Hudson, R.G. "Some Physicochemical Criteria for the Selection of Carbides as Cathodes in Cesium Thermionic Converters," in Metallurgy of Semiconductor Materials, J. B. Schroeder, Ed., Interscience Publishers, N.Y. (1962).
6. Yang, L. and Carpenter, F. D., J. Electrochem Soc., 108, 1079 (1962).
7. Horner, M. H., Weinberg, A. F., and Yang, L., "Compatibility of Uranium-Bearing Nuclear Fuels and Refractory Metal Thermionic Emitters," Proc. of Thermionic Specialists Conference, Gatlinburg, Tennessee, October 1963. Available from the authors.
8. Ackermann, R. J., Thorn, R. J., and Gilles, P., J. Chem. Phys. 25, 1089-1097 (1956).
9. Hausner, H., Grain Growth of UO₂, Part 1, GEAP-4315 (1963). Available from OTS, Dept. of Commerce, Washington 25, D.C.
10. Martin, A. E. and Edwards, K. E., J. Phys. Chem. 69, 1788 (1965).
11. Edwards, J. W., Johnston, H. L., and Blackburn, P. E., J. Am. Chem. Soc. 74, 1539 (1952).
12. Roberts, L. E. J. and Walter, A. J., J. Inorg. Nucl. Chem. 22, 213 (1961).
13. Aronson, S. and Belle, J., J. Chem. Phys. 29, 151 (1958).
14. King, E. G., Weller, W. W., and Christensen, A. V., "Thermodynamics of Some Oxides of Molybdenum and Tungsten," U. S. Bureau of Mines Report RI-5664 (1960).
15. Rapp, R. A., Trans. AIME 227, 371 (1963).
16. Rothwell, J., J. Nuc. Mtl. 6, 229 (1962).
17. Anderson, et. al., Nature 105, 916 (1960).
18. Kaznoff, A.I. and Weidenbaum, B., "Nuclear Fuel, Cladding, and Insulators for Thermionic Converters," at Materials Associated with Direct Energy Conversion Conference, London, June 1965.